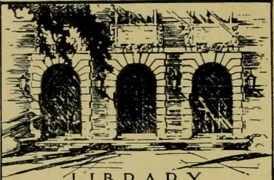

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IRA REMSEN

PROFESSOR OF CHEMISTRY IN THE JOHNS HOPKINS UNIVERSITY.

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Contributions from the Chemical Laboratory of Harvard College.

XCVI.—ON PARABROMDIMETANITROTOLUOL AND SOME OF ITS DERIVATIVES.[1]

BY C. LORING JACKSON AND MARTIN H. ITTNER.

The work described in this paper was undertaken in order to study the behavior of a bromine atom in the ortho position between two nitro groups, but not exposed to the loosening action of a third negative group in the para position. We hoped in this way to settle two points: the ease with which an atom of bromine thus situated could be removed, and whether it might be replaced by an atom of hydrogen under the influence of sodium malonic ester, or sodic ethylate, as has been frequently observed in this laboratory[2] in the study of more highly substituted aromatic compounds.

In selecting the compound with the desired constitution we hesitated between the bromdinitrobenzol ($Br1.NO_2 2.NO_2 6$) and the bromdinitrotoluol ($CH_3 1.Br4.NO_2 3.NO_2 5$), and selected the latter, because it was somewhat more easily prepared than the benzol compound. This selection proved an unfortunate one, so far as the first object of our research is concerned, since the parabromdimetanitrotoluol proved itself a not very reactive body. C. A. Lobry de Bruyn[1] has found that in many cases the presence of a methyl group attached to the benzol ring prevents the replacement of a nitro group by an alkoxyl radical. In other words, that the methyl in toluol and its higher homologues exercises a protective action upon nitro groups, which would otherwise be easily replaced. The inertness of our parabromdimetanitrotoluol is probably, therefore, due to a similar protective action of the methyl radical upon the atom of bromine rather than to the constitution of the molecule, although this question cannot be settled until the vicinal bromdinitrobenzol has been submitted to a similar investigation.

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[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the Degree of Doctor of Philosophy, by Martin H. Ittner.

[2] This JOURNAL, **11**, 93, 541; **12**, 7, 164, 289; **13**, 164: **15**, 607.

The parabromdimetanitrotoluol was made by the reaction of Griess from the dinitrotoluidine, melting at 166°, of Beilstein and Kuhlberg.[2] It was also made by the action of nitric acid on brommetanitrotoluol, but this reaction gave much less good results than that mentioned at first. The substance melts at 118°, and is easily converted by warm aniline into the anilidodinitrotoluol, $C_6H_2C_6H_5NH(NO_2)_2CH_3$, melting-point 169°. (The nitroso derivative of this compound, $C_6H_2(C_6H_5NNO)(NO_2)_2CH_3$, melts at 123°). Sodium malonic ester did not act upon the bromdinitrotoluol under any conditions we could find although we tried the experiment under a great variety of temperatures and for different lengths of time. With sodic ethylate, on the other hand, it gave such a striking color reaction that we have decided to describe the product and those similar to it derived from allied substances in a separate paper. We will only remark here that no dinitrotoluol could be detected in the products of this reaction, and that therefore there is no evidence that the atom of bromine is replaced by hydrogen under these conditions. In fact we have not as yet found any signs of this reaction except in substances containing three or more atoms of halogen. With ammonic hydrate the bromdinitrotoluol gives dinitrotoluidine, melting at 166°; with sodic hydrate dinitrokresol, melting at 85°.

We next turned our attention to the parabromdimetanitrobenzoic acid, $C_6H_2Br(NO_2)_2COOH$, which we made by the oxidation of the corresponding toluol. It melts at 181°, and, as was to be expected, is much more reactive than the parabromdinitrotoluol, since the atom of bromine is exposed to the loosening effects of the two nitro groups in the ortho position and a carboxyl group in the para position. Thus sodic hydrate in the cold converts it after some time into the corresponding oxydinitrobenzoic acid, melting at 245°–246°. We must pause here to remark that H. Salkowski[1] gives the melting-point of this paroxydimetanitrobenzoic acid as 235°–237°, but that we have proved the melting-point 245°–246° is the correct one by preparing the acid in four different ways, two of which are those given by Salkowski. With ammonic hydrate upon standing the bromdinitrobenzoic acid gives chrysanisic acid, recognized by its melting-point 259°. With aniline gently warmed a new acid was formed, the anilidodinitrobenzoic acid, $C_6H_2(C_6H_5NH)(NO_2)_2COOH$, which melts at 239°. With sodium malonic ester, at ordinary temperatures, the bromdinitrobenzoic acid was converted into the dinitrocarboxylphenylmalonic ester,

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[1] Rec. Trav. Chim. Pays. Bas., **14**, 95.

[2] Ann. Chem. (Liebig), **158**, 342.

$$C_6H_2CH(COOC_2H_5)_2(NO_2)_2COOH,$$

which melts at 176°. In none of these experiments was the formation of dinitrobenzoic acid observed.

The new acids mentioned above were further characterized by the analysis of the following salts:

$$C_6H_2Br(NO_2)_2COONa.4H_2O;$$
$$C_6H_2Br(NO_2)_2COOAg;$$
$$C_6H_2C_6H_5NH(NO_2)_2COONa.3H_2O;$$
$$(C_6H_2C_6H_5NH(NO_2)_2COO)_2Ca.7H_2O;$$
$$C_6H_2CAg(COOC_2H_5)_2(NO_2)_2COONH_4.$$

The esters were also prepared, $C_6H_2Br(NO_2)_2COOC_2H_5$, melting at 105°, and $C_6H_2C_6H_5NH(NO_2)_2COOC_2H_5$, melting at 154°. It is perhaps worth mentioning that both these esters were made easily by the action of hydrochloric acid on the alcoholic solution, as would be expected from the recent work of Victor Meyer. The anilidodinitrobenzoic acid gave no nitroso compound with nitrous acid, whereas the anilidodinitrotoluol gave such a compound without difficulty, as has been mentioned already.

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[1] Ann. Chem. (Liebig), 163, 36.

Some experiments on the effect of the complexity of molecules upon the properties of the substances may be mentioned here, although they did not lead to such definite results as we had hoped. Our plan was to start from the anilidodinitrotoluol, which we converted into a tribrom compound, melting at 238°, and then by making a nitro compound from this and treating it with aniline, we hoped to obtain an anilidodibromdinitranilidodinitrotoluol,

$$C_6H_5NHC_6HBr_2(NO_2)_2NHC_6H_2(NO_2)_2CH_3,$$

and by repeating these reactions to increase the chain of benzol rings indefinitely. Unfortunately the substances ceased to be crystalline very early in this work, since we could obtain crystals neither from the nitrotribrom compound, the anilido compound made from that, nor the bromanilido compound formed from the last by the action of bromine. Whether this tendency to appear in an amorphous form is due to the increasing complexity of the molecule (three benzol rings), or to peculiarities in this class of compounds can be determined only by more extended experiments. In another attempt to study this subject the amidophenylenimidodinitrotoluol, $NH_2C_6H_4NHC_6H_2(NO_2)_2CH_3$, was prepared by the action of metaphenylenediamine on bromdinitrotoluol. The reaction is much more violent than that with aniline, in fact, if no diluent is used, most of the product is charred. The substance melts at 185°, and gave a tribrom compound melting at 222°. We could not succeed in replacing the amido group by an atom of bromine.

The action of pyridine on the bromdinitrobenzoic acid was also studied. This gave two products: a white salt of pyridine, undoubtedly having the following formula, although it was too unstable to allow a good analysis,

$$C_6H_2Br(NO_2)_2COOHC_5H_5N,$$

and a yellow substance, which decomposed so easily that we were unable to analyze it. Its nature can, however, be determined from its properties and decompositions. In the first place, as it was obtained by the action of pyridine on the white salt, it probably contains more pyridine than this substance. Its solubility in water indicates that it is a salt, and this inference is confirmed by its conversion into a red silver salt, and by the fact that pyridine is set free from it by alkalies. When crystallized from common alcohol the yellow body is slowly converted into bromide of pyridine and paroxydimetanitrobenzoic, melting-point 245°–246°. The easy solubility of pyridine bromide in alcohol proves that the yellow body could not be a mixture of this substance and oxydinitrobenzoic acid. The best explanation of the observed facts which we have been able to find is that in this substance the radical, $C_6H_2Br(NO_2)_2$, of the benzoic acid forms a salt with pyridine just as hydrobromic acid does, Br and $—C_6H_2(NO_2)_2$ combining with the atom of nitrogen. We should therefore ascribe to this substance the formula,

$$C_5H_5NBrC_6H_2(NO_2)_2COOHC_5H_5N,$$

considering it a sort of double salt of pyridine, which, when crystallized from ordinary alcohol, would break up with the water present into oxydinitrobenzoic acid, pyridine bromide and pyridine. Auwers[1] has obtained a similar addition-product from pyridine and his tribrompseudocumenol, but it seems to be somewhat more stable than ours, as it must be boiled with water in order to convert it into pyridine, hydrobromic acid and oxydibromcumenol.

We have also prepared the chlordinitrobenzoic acid which melts at 159°; and some preliminary work on the action of hydrochloric acid in a sealed tube on bromdinitrobenzoic acid showed that the products were dinitrophenol ($OH\,1$, $NO_2 2$, $NO_2 6$), oxydinitrobenzoic acid and perhaps the as yet undescribed vicinal bromdinitrobenzol.

All the substances mentioned in this paper are derived from the bromdinitrotoluol, ($CH_3 1$, $Br 4$, $NO_2 3$. $NO_2 5$), by simple reactions, and therefore have a constitution similar to that substance.

EXPERIMENTAL PART.

Preparation of Dinitrotoluidine.

The dimetanitroparatoluidine which served as the starting-point of all our work was prepared according to the method of Beilstein and Kuhlberg,[1] but as we have introduced some alterations in the details of the process we think it best to give it in full as carried on by us. Paracettoluid was dropped in small portions at a time into well cooled nitric acid, of specific gravity 1.5 or over (obtained by distilling nitre and sulphuric acid in the proportion of 1 molecule of each). A weaker acid gave a considerable amount of mononitracettoluid. In this way we obtained an average yield of the crude dinitracettoluid, amounting to 75 per cent. of that required by the theory. The least carelessness, either in cooling the acid or in the addition of the acettoluid, reduced the yield very considerably, but in no case did we succeed in raising it much above 75 per cent. That we had formed the dinitracettoluid of Beilstein and Kuhlberg was proved by recrystallizing a little of it from alcohol, when it showed the melting-point of 191° given by them.

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[1] Ber. d. chem. Ges., **28**, 2893, 2912.

For the subsequent work this purification was unnecessary, so the crude dinitracettoluid was dried and then boiled with sulphuric acid of specific gravity 1.44 in a flask with a return condenser. The saponification took place very quickly after the acid had reached its boiling-point and could be followed by the change in color from yellowish-brown to dark-brown. When it was complete, the liquid was cooled in running water, diluted somewhat, and filtered; the impurities ran through, leaving nearly pure dinitrotoluidine on the filter, which, after recrystallization from alcohol, showed the melting-point, 166°, given by Beilstein and Kuhlberg. The yield was not far from quantitative. This saponification with sulphuric acid is to be preferred to that with alcoholic potash used by Beilstein and Kuhlberg, because it gives a better yield and a purer product, since the decomposition of the dinitracettoluid by the alkali is avoided, which, as Wagner[2] has found, converts it partially into dinitrokresol, and also brings about a more complete decomposition attended by the formation of potassic cyanide. Another advantage in the use of the sulphuric acid is that it dissolves any mononitrotoluidine which may be present, thus avoiding the treatment of the saponified product with hydrochloric acid for this purpose, as recommended by Beilstein and Kuhlberg.

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[1] Ann. Chem. (Liebig), **158**, 342.

[2] Ber. d. chem. Ges., **7**, 536.

Parabromdimetanitrotoluol, $C_6H_2Br(NO_2)_2CH_3$.

This substance was prepared as follows: A quantity of the dry dinitrotoluidine was suspended in a concentrated solution of hydrobromic acid (specific gravity 1.44) and treated from time to time with small quantities of sodic nitrite, until a large excess of this reagent had been added. During this operation the liquid was kept well cooled, and the mouth of the flask was loosely corked to prevent as far as possible the escape of nitrous fumes. Since the diazo compound formed is as insoluble in hydrobromic acid as the dinitrotoluidine itself, the reaction takes place very slowly, so that it was found advisable to let small quantities of the dinitrotoluidine stand with the solution of nitrous acid for at least two days, while large quantities needed a week or more, with occasional addition of sodic nitrite and shaking. This very slow formation of the diazo compound and its insolubility probably account for the statement of Beilstein and Kuhlberg,[1] that nitrous anhydride does not act on dinitrotoluidine at ordinary temperatures. After the mixture had stood long enough, more hydrobromic acid was added, if necessary, and then the liquid was heated, care being taken to keep the contents of the flask well stirred, and to regulate the heat so that the solid portions should not melt, as, if these precautions were neglected, a smaller yield was obtained, and the product was mixed with impurities, which it was hard to remove. The product was at first purified by crystallizing it from alcohol, but later it was found that nitric acid of specific gravity 1.36 did not act on the bromdinitrotoluol, while it did oxidize the impurities, and this observation was used to improve greatly the method of purification. The crude product accordingly was treated with enough nitric acid (specific gravity 1.36) to dissolve it when boiling, and the mixture boiled until nitrous fumes ceased to come off, which indicated that all the impurities had been oxidized. The hot acid solution was then allowed to cool, when the bromdinitrotoluol crystallized out in white prisms, which, after washing with sodic hydrate and water, were pure, if the amount of impurity in the crude substance had not been excessive. Or the nitric acid solution was precipitated with water, and, after washing with sodic hydrate and water, the precipitate recrystallized from alcohol. The substance, in whichever way purified, showed the constant melting-point 118°. It was dried at 100° and analyzed with the following results :

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[1] Ann. Chem. (Liebig), **158**, 344.

I. 0.1640 gram of the substance gave, by the method of Carius, 0.1185 gram of argentic bromide.

II. 0.2100 gram of the substance gave 0.1518 gram of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2CH_3$.	Found. I.	II.
Bromine	30.66	30.76	30.76

131 grams of the dinitrotoluidine gave 150 grams of pure bromdinitrotoluol instead of the 174 grams required by the theory, that is, a yield of 86 per cent. The yield varied between this and 75 per cent. in different preparations.

Properties of Parabromdimetanitrotoluol.—It crystallizes from nitric acid in white prisms apparently belonging to the trimetric system ; from alcohol at first in slender curving needles somewhat branched ; later these needles spread out into curving groups of rather irregular plates united by their edges, and if the plates are very well developed, rectangular forms are observed in them. It melts at 118°. It is very soluble in acetone, or ethyl acetate ; freely soluble in benzol, chloroform, or carbonic disulphide ; moderately soluble in ethyl, or methyl alcohol, or glacial acetic acid, and its solubility in these three solvents is increased by heat ; nearly insoluble in water, or cold ligroïn, moderately soluble in hot ligroïn. The best solvent for it is strong hot nitric acid or a mixture of benzol and ligroïn. Insoluble in strong hydrochloric acid whether cold or hot ; insoluble in cold, soluble in hot nitric acid, or in sulphuric acid.

The parabromdimetanitrotoluol is a fairly reactive substance so far as the bromine which it contains is concerned. Cold ammonic hydrate has no action upon it, but a boiling solution of aqueous ammonic hydrate converts it into dinitrotoluidine, which was recognized by its melting-point, 166°. When mixed with a cold solution of sodic hydrate, there is also no action, but, if the mixture is heated, the bromdinitrotoluol is slowly converted into the dinitrokresol melting at 85°. A boiling aqueous solution of sodic carbonate produces the same effect, but even more slowly. With sodic ethylate it gives a brilliant blue compound which, however, is very unstable. The behavior of other reagents, which led to new compounds, is described in some of the following sections of this paper.

Many attempts were made to introduce bromine into the side chain of the bromdinitrotoluol, but none led to the desired result. In fact the stability of this substance toward bromine is remarkable, as shown by the following experiment: Five grams of bromdinitrotoluol were heated with a large excess of bromine in a flask, with a return-condenser fitted to it by means of a plug of asbestos, to a temperature of 200°–210°, by means of an oil-bath, the contents of the flask being at the same time exposed to full sunlight. The heating was continued for five days, but in all this time no evolution of hydrobromic acid was observed, and at the end of the experiment almost the whole of the bromdinitrotoluol was recovered unaltered. The small amount which was acted on seemed to be completely decomposed, as no other compound could be isolated.

The same bromdinitrotoluol was also prepared from parabrommetanitrotoluol made from mononitrotoluidine (melting-point 114°) by Sandmeyer's reaction. For this purpose the bromnitrotoluol (which had not been brought into the solid state) was slowly added to about five times its weight of nitric acid of specific gravity 1.52, in which it dissolved easily and quietly. The solution was heated on the steam-bath for about ten minutes, and then poured into cold water. The white precipitate thus obtained after a somewhat tedious purification by crystallization from alcohol showed the constant melting-point 118°. The mother-liquors yielded a liquid which probably was unaltered bromnitrotoluol, but may have contained an isomeric dinitro compound. This method of preparing bromdinitrotoluol is far inferior to that for making it from dinitrotoluidine.

Action of Aniline on Bromdinitrotoluol.

The bromdinitrotoluol was dissolved in an excess of aniline with the aid of a little heat, when a reaction took place, the product of which was obtained by removing the unaltered aniline and the aniline bromide formed with hydrochloric acid and water. The residue was then purified by crystallization from a mixture of benzol and alcohol, until it showed the constant melting-point 169°, when it was dried at ordinary temperatures and analyzed with the following result:

0.2000 gram of the substance gave 27.0 cc. of nitrogen at a temperature of 24° and a pressure of 759 mm.

	Calculated for $C_6H_2C_6H_5NH(NO_2)_2CH_3$.	Found.
Nitrogen	15.38	15.16

The substance is, therefore, paranilidodimetanitrotoluol, formed by replacing the atom of bromine by the anilido group. The yield was essentially quantitative.

Properties of Paranilidodimetanitrotoluol.—It crystallizes from a mixture of benzol and alcohol in long, very slender, much branched, orange needles. It melts at 169°. It is very soluble in chloroform or acetone; freely soluble in carbonic disulphide or ethyl acetate, much more soluble in the latter when hot; soluble in ether; slightly soluble in cold ethyl or methyl alcohol, in benzol, or in glacial acetic acid; more soluble in these three solvents when they are hot; almost insoluble in water or ligroïn. The best solvent for it is a mixture of benzol and alcohol. Strong nitric acid (sp. gr. 1.36) converts it into a yellow substance, probably a nitro compound; strong sulphuric acid dissolves it in the cold apparently without change. It is insoluble in an aqueous solution of sodic hydrate. With sodic ethylate it gives an unstable green compound.

An unsuccessful attempt was made to obtain the anilidodinitrotoluol described above by the action of dinitrotoluidine on aniline chloride according to the method used in getting diphenylamine from aniline and aniline chloride. For this purpose 2.0 grams of dinitrotoluidine mixed with the chloride from 0.93 gram of aniline and 50 cc. of water were heated over night to 200°–210° in a sealed tube. Upon examining the contents of the tube no anilidodinitrotoluol could be detected. Most of the dinitrotoluidine was recovered unaltered, but part of it had been completely charred, apparently by the hydrochloric acid of the aniline chloride, as the aniline was found in the free state. This result makes it probable that no reaction of the sort desired takes place with these substances.

Nitrosoanilidodinitrotoluol, $C_6H_2C_6H_5NNO(NO_2)_2CH_3$.

This substance was prepared as follows: Five grams of anilidodinitrotoluol were mixed in a flask with 30 cc. of benzol and about 50 cc. of hydrochloric acid. Part of the substituted toluol dissolved in the benzol, and the rest remained suspended in this solution, which floated on the hydrochloric acid. Small pieces of sodic nitrite were then introduced from time to time into the mixture, which was kept well cooled throughout the process. The nitrous fumes in escaping through the benzol solution converted the anilido into the nitroso compound, all of which went into solution in the benzol, when the process was complete. The contents of the flask were then poured into a large beaker, diluted with water and freed from benzol by blowing a stream of air over the surface of the liquid. The solid residue deposited from the benzol sank to the bottom of the beaker, and was filtered out. As thus obtained it was practically pure, but for greater precaution it was crystallized from chloroform. It melted constant at 123°, and was analyzed with the following result:

0.2000 gram of the substance gave 32.42 cc. of nitrogen at a temperature of 19°.5 and a pressure of 762.5 mm.

	Calculated for $C_6H_2C_6H_5NNO(NO_2)_2CH_3$.	Found.
Nitrogen	18.54	18.58

The yield is essentially quantitative.

Properties of Nitrosoanilidodinitrotoluol.—Crystallized from chloroform it appears in good-sized rhombic plates, probably of the trimetric system. It is colorless to pale yellow. It melts at 123°, decomposing with evolution of much gas; this decomposition also takes place at lower temperatures, as the substance blackens on account of it, if heated for a short time in the steam-bath, or if heated for a longer time to temperatures below 100°. It is very soluble in benzol, toluol, acetone, chloroform, or carbonic disulphide; freely soluble in glacial acetic acid or ethyl acetate; soluble in ethyl or methyl alcohol, or in ether; slightly soluble in ligroïn; essentially insoluble in water, whether hot or cold. The best solvent for it is cold chloroform. In crystallizing it, heating the solutions should be avoided, as this is apt to bring about decomposition. It gives no colored compound with sodic ethylate.

Bromdinitrotoluol and Sodium Malonic Ester.

A number of attempts were made to prepare a malonic ester derivative from the bromdinitrotoluol, but in no case with success. The action of the sodium malonic ester on the bromdinitrotoluol was tried at ordinary temperatures, at 0°, with a boiling solution of ethyl alcohol, with a boiling solution of amyl alcohol, but in all these cases nearly the whole of the bromdinitrotoluol was recovered unaltered. The only new product, when there was one, occurred in the shape of a tarry mass, amounting to a few per cent. of the total weight, which we ascribe to the action of a slight excess of the sodic ethylate used in making the sodium malonic ester. We infer, therefore, that sodium malonic ester does not act on bromdinitrotoluol, and this inference is confirmed by the fact that we saw no signs of one of the red salts so characteristic of the substituted malonic esters of this class.

Parabromdimetanitrobenzoic Acid, $C_6H_2Br(NO_2)_2COOH$.

In trying to oxidize the bromdinitrotoluol with nitric acid we found that it was entirely unaffected either by dilute nitric acid or the ordinary strong acid of sp. gr. 1.36 in open vessels. In fact we founded a method of purifying the bromdinitrotoluol on this property, as has been already stated. By heating the bromdinitrotoluol in a sealed tube with strong nitric acid, a mixture of bromdinitrobenzoic acid and the unaltered toluol was obtained, but this inconvenient method of oxidation was abandoned for the action of potassic dichromate and sulphuric acid. We proceeded, therefore, as follows: The bromdinitrotoluol was boiled for eight hours in a flask with a return-condenser with an excess of potassic dichromate and sulphuric acid diluted with an equal volume of water. If the oxidation was complete, colorless rhombic plates of the acid separated from the solution when it was allowed to cool slowly. These were filtered out on a platinum cone, washed free from sulphuric acid with a little water and dried, when they were found to be pure. The acid filtrate gave no precipitate on the addition of water. On one occasion a portion of the diluted filtrate was extracted with benzol, but the amount of acid obtained was so small that this extraction was not used again. If the oxidation of the bromdinitrotoluol had not taken place completely, as was sometimes the case, the unaltered substance which remained melted in the liquid during the boiling, solidified when the liquid cooled in lumps, which were easily picked out from the loose crystals of the acid. By treating these lumps with a cold solution of sodic carbonate, the bromdinitrobenzoic acid was converted into its sodium salt and dissolved. The unaltered bromdinitrotoluol was then filtered out, and the sodium salt purified by recrystallization. The pure acid as obtained directly from the oxidation melts at 181°. It was dried at 100° and analyzed with the following result:

0.1670 gram of the substance gave, by the method of Carius, 0.1081 gram of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2COOH$.	Found.
Bromine	27.50	27.54

The bromdinitrotoluol gave, by the process just described, about its own weight of the bromdinitrobenzoic acid, that is, about 90 per cent. of the theoretical yield.

Properties of Bromdinitrobenzoic Acid.—The substance crystallizes from dilute sulphuric acid in colorless rhombic plates or flat prisms. On evaporating a solution of the acid in alcohol to dryness on the water-bath a syrup was obtained, which on long standing deposited three monoclinic prisms, one of which was nearly 2 cm. long. Unfortunately a slight rise in temperature of the room caused these crystals to redissolve before they could be removed and their identity established by a melting-point determination, and we have never succeeded in getting such crystals again. We feel little doubt, however, that these were crystals of the acid. It melts at 181°. It is very soluble in ethyl or methyl alcohol, in ether, ethyl acetate, or acetone; freely soluble in benzol, glacial acetic acid, or chloroform; moderately soluble in carbonic disulphide; slightly soluble in cold ligroïn, somewhat more soluble in hot; slightly soluble in water. The best solvent for it is a mixture of benzol and ligroïn. It is insoluble in hydrochloric acid whether cold or hot; insoluble in nitric or sulphuric acid in the cold, somewhat soluble in either when hot, and can be obtained unchanged from these solutions.

The bromdinitrobenzoic acid is a very reactive substance; a cold dilute solution of sodic hydrate dissolves it, forming the sodium salt described below, but, if the solution of the salt is allowed to stand some time in the cold with sodic hydrate, the atom of bromine is replaced by hydroxyl, and the disodium salt of the oxydinitrobenzoic acid melting at 245°–246° is formed. The same reaction takes place rapidly if the two reagents are heated together. Sodic carbonate in cold aqueous solution forms the salt of the bromdinitrobenzoic acid, but does not act further upon it. When sodic carbonate is heated with the acid, the disodic salt of the oxydinitrobenzoic acid is formed, as in the case of sodic hydrate. Ammonic hydrate in the cold forms the ammonium salt of bromdinitrobenzoic acid, but on standing with an excess of ammonic hydrate this is converted into ammonic chrysanisate by the replacement of the bromine by the amido group. This was proved by the melting-point, 259°, of the acid formed. Sodic ethylate gives with the bromdinitrobenzoic acid an intense reddish-purple color, which served as a very delicate and distinctive test for the presence of bromdinitrobenzoic acid.

Metaphenylenediamine gave an amidophenylimido compound, which was not further studied.

Sodic Bromdinitrobenzoate, $C_6H_2Br(NO_2)_2COONa.4H_2O$.—A quantity of bromdinitrobenzoic acid was mixed with a slight excess of sodic carbonate, hot water was added, and the mixture warmed until the acid had dissolved. The heating was not continued longer than was absolutely necessary, as the salt decomposed when its solution was heated. As the hot solution cooled, crystals were deposited in large quantity, which were filtered out, and purified by one crystallization from water. The sodic bromide and sodic oxydinitrobenzoate formed by the decomposition of the bromdinitrobenzoic acid were contained principally in the mother-liquor from the first crystals. The substance separated by acidification from the mother-liquors of the second crystallization was essentially pure bromdinitrobenzoic acid. The salt was accordingly analyzed as follows:

I. 0.5874 gram of the air-dried salt lost 0.1097 gram of water when dried at 110°.

II. 0.4437 gram of air-dried salt lost 0.0832 gram of water when dried at 110°.

	Calculated for $C_6H_2Br(NO_2)_2COONa.4H_2O$.	Found. I.	II.
Water	18.70	18.68	18.75

I. 0.4777 gram of the salt dried at 110° gave 0.1053 gram of sodic sulphate.

II. 0.3605 gram of the salt dried at 110° gave 0.0800 gram of sodic sulphate.

	Calculated for $C_6H_2Br(NO_2)_2COONa$.	Found. I.	II.
Sodium	7.35	7.14	7.19

The sodic bromdinitrobenzoate crystallizes in fine needles, which are white with a faint tinge of straw-color. It is moderately soluble in cold water, very readily soluble in hot water. If the solution is heated for some time, sodic bromide and oxydinitrobenzoic acid are formed. A similar decomposition takes place more rapidly with an excess of alkali. In fact, with sodic hydrate this change will go on even in the cold.

Argentic Bromdinitrobenzoate, $C_6H_2Br(NO_2)_2COOAg$.—This substance was obtained from a solution of the ammonium salt made as follows: Some bromdinitrobenzoic acid was treated with ammonic hydrate in the proportion of 1 molecule of each substance. The ammonic hydrate solution was made so dilute that all the salt formed was in solution. To this solution a concentrated solution of argentic nitrate was added, and the whole was thoroughly stirred, when a copious white precipitate made up of fine needles was thrown down. This was filtered out, washed with a little water, dissolved in dilute alcohol, filtered once more, and allowed to crystallize. The crystals thus obtained were dried by exposure to the air, and then heated to 100°, when they were found to suffer no loss of weight, and were accordingly analyzed with the following result:

0.1978 gram of the salt gave, by heating in a sealed tube with nitric acid and a crystal of potassic bromide, 0.0927 gram of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2COOAg$.	Found.
Silver	27.13	26.91

The silver salt crystallizes from dilute alcohol in bunches of dull gray needles. Just after it is formed it is very appreciably soluble in water, but it grows less soluble on standing, and after it has been dried is almost insoluble in water. When first precipitated the salt is white.

We also studied the behavior of an aqueous solution of sodic bromdinitrobenzoate with salts of all the common basic radicals. Of these only four produced precipitates including argentic nitrate, the action of which has just been described.

Ferric chloride gave a heavy white precipitate slightly soluble in cold, more soluble in hot water.

Plumbic acetate gave a precipitate similar to the preceding in appearance and solubility.

Cupric sulphate gave a light green precipitate, more soluble than the others.

Ethyl Ester of Bromdinitrobenzoic Acid, $C_6H_2Br(NO_2)_2COOC_2H_5$.—Five grams of bromdinitrobenzoic acid were dissolved in about 25 cc. of absolute alcohol and the solution was saturated with dry hydrochloric acid gas. During the saturation much of the ester was precipitated, as it is less soluble in alcohol than the acid. In order to complete the reaction the mixture was allowed to stand over night, and then poured into water, after which the precipitated ester was filtered out, and purified by crystallization from alcohol, until it showed the constant melting-point, 105°, when it was dried and analyzed with the following result:

0.2227 gram of the substance gave, by the method of Carius, 0.1307 gram of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2COOC_2H_5$.	Found,
Bromine	25.08	24.96

Properties of the Bromdinitrobenzoic Ethyl Ester.—It crystallizes from alcohol in fine short white needles, which melt at 105°. It is very soluble in benzol, toluol, chloroform, acetone, or ethyl acetate; easily soluble in ether; moderately soluble in alcohol, carbonic disulphide, or glacial acetic acid, much more soluble in these solvents when they are hot; almost insoluble in cold ligroïn, slightly soluble in it when hot; insoluble in water. By crystallization from ordinary alcohol the ester is slowly converted into the corresponding acid. Cold sodic or ammonic hydrate in aqueous solution does not affect it, but either of these reagents when hot saponifies it, and the same effect is produced by hot dilute acids. An alcoholic solution of sodic ethylate gives an intense rose color with it, very similar to the color of eosine, but on standing this gradually changes to a reddish purple on account of the saponification of the ether.

Some experiments were tried with the purpose of preparing parabromdimetanitrobenzoic acid by Griess's reaction from chrysanisic acid. H. Salkowski states[1] that he was unable to obtain a diazo compound from chrysanisic acid in the cold, and we can confirm this observation, as in one experiment a mixture of chrysanisic acid (made by oxidation of dinitrotoluidine according to Frederici[2]) and hydrobromic acid was submitted to the action of nitrous anhydride for over two months, and no reaction could be observed. This negative result is the more conclusive, because we possessed in sodic ethylate a reagent by which even a trace of bromdinitrobenzoic acid could be detected with certainty. On the other hand, Salkowski[3] succeeded in making oxydinitrobenzoic acid from chrysanisic acid by acting on it with nitrous acid in presence of boiling dilute acids, and accordingly we proceeded as follows: One gram of chrysanisic acid was mixed with a solution of hydrobromic acid of specific gravity 1.44, the mixture heated to boiling, and small pieces of sodic nitrite added from time to time. After about half an hour of this treatment all the chrysanisic acid had passed into solution, but that it had not been completely converted into bromdinitrobenzoic acid was shown by the strong yellow color of the liquid, which was not removed by further addition of sodic nitrite. The solution was now poured into cold water, and on standing a few faintly yellow crystals were deposited, which melted a little below the melting-point of bromdinitrobenzoic acid. The quantity was too small to raise the melting-point by crystallization, but we established its identity by the following tests. Some of the substance gave with an alcoholic solution of sodic ethylate the characteristic reddish purple color of the bromdinitrobenzoic acid. By treatment with aniline it was converted into orange-red needles, which melted at 235°–6°, instead of 239°, the melting-point of anilidodinitrobenzoic acid, and showed with sodic ethylate the pansy-purple color characteristic of it. This method of preparing bromdinitrobenzoic acid is inferior to that for making it from bromdinitrotoluol, since it gives a very small yield, and a tedious purification would be necessary to get rid of the unaltered chrysanisic acid.

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[1] Ann. Chem. (Liebig), **163**, 34.

[2] Ber. d. chem. Ges., **11**, 1976.

[3] Ann. Chem. (Liebig), **163**, 36.

Anilidodinitrobenzoic Acid, $C_6H_2C_6H_5NH(NO_2)_2COOH$.—This substance was prepared by warming some bromdinitrobenzoic acid with a slight excess of aniline. As soon as the acid had dissolved the mixture was allowed to cool, and, after removing the excess of aniline with hydrochloric acid and water, the residue was purified by crystallization from a mixture of benzol and alcohol until it showed the constant melting-point, 239°, when it was dried at 100° and analyzed with the following result:

0.2001 gram of the substance gave 23.7 cc. of nitrogen at a temperature of 15° and a pressure of 749 mm.

	Calculated for $C_6H_2C_6H_5NH(NO_2)_2COOH$.	Found.
Nitrogen	13.86	13.67

Properties of Anilidodinitrobenzoic Acid.—It crystallizes from a mixture of benzol and alcohol in orange needles or slender prisms, terminated by a single plane at an oblique angle. It melts at 239°. It is very soluble in ether, acetone, glacial acetic acid, or ethyl acetate; moderately soluble in cold chloroform, more soluble in hot; slightly soluble in benzol, or ethyl alcohol when cold, fairly soluble in either when hot; more soluble in methyl than in ethyl alcohol; slightly soluble in carbonic disulphide, or ligroïn; essentially insoluble in water. Cold hydrochloric acid or nitric acid does not dissolve it, but with hot nitric acid it goes into solution, and water precipitates what seems to be a new compound. It dissolves unchanged in cold sulphuric acid. Alkalies and alkaline carbonates dissolve it, forming salts. With a cold concentrated solution of sodic hydrate it gives a purple color similar to that of a dark pansy, which changes in a few minutes to a greenish-brown. Sodic ethylate gives the same color, which in this case is more permanent. When boiled with a strong solution of sodic hydrate aniline is set free, and the oxydinitrobenzoic acid, melting at 245°–246°, is formed. At the same time a considerable amount of phenylisocyanide is evolved.

Sodic Anilidodinitrobenzoate, $C_6H_2C_6H_5NH(NO_2)_2COONa.3H_2O$.—This salt was made by boiling the acid with an aqueous solution of an excess of sodic carbonate, until it had dissolved, which took several hours. The solution was then concentrated, when, upon cooling, it deposited crystals of the salt, which were purified by recrystallization from water, after which it was analyzed with the following results:

I. 0.5867 gram of the air-dried salt when dried at 100° lost 0.0828 gram of water.

II. 0.3487 gram of the salt dried in air lost when dried *in vacuo*, over sulphuric acid, 0.0493 gram of water.

	Calculated for $C_6H_2C_6H_5NH(NO_2)_2COONa.3H_2O$.	Found. I.	II.
Water	14.25	14.11	14.14

The substance, therefore, contains 3 molecules of water of crystallization, which it loses *in vacuo*.

I. 0.2104 gram of the salt dried at 100° gave 0.0460 gram of sodic sulphate.

II. 0.2998 gram of the salt dried at 100° gave 0.0653 gram of sodic sulphate.

	Calculated for $C_6H_2C_6H_5NH(NO_2)_2COONa$.	Found. I.	II.
Sodium	7.08	7.08	7.06

The salt forms orange-red needles and is freely soluble in water.

Calcic Anilidodinitrobenzoate, $(C_6H_2C_6H_5NH(NO_2)_2COO)_2Ca.7H_2O$.—This salt was made by boiling the acid with calcic carbonate and water for two days. At the end of this time the solution of the salt was filtered off from the excess of calcic carbonate and a little unaltered acid. The filtrate was then concentrated and set aside to crystallize, when the crystals were analyzed with the following results:

I. 0.4050 gram of the air-dried salt, when dried at 100°, lost 0.0359 gram of water.

II. 0.2991 gram of the air-dried salt, when dried at 100°, lost 0.0264 gram of water.

	Calculated for $(C_6H_2C_6H_5NH(NO_2)_2COO)_2Ca.7H_2O$.	Found. I.	II.
Water	8.91	8.86	8.83

I. 0.3691 gram of the salt, dried at 100°, gave 0.0773 gram of calcic sulphate.

II. 0.2727 gram of the salt, dried at 100°, gave 0.0572 gram of calcic sulphate.

	Calculated for $(C_6H_2C_6H_5NH(NO_2)_2COO)_2Ca$.	Found. I.	II.
Calcium	6.21	6.16	6.17

The salt when dried *in vacuo* over sulphuric acid loses only two of its molecules of water of crystallization, as is shown by the following results, although a larger amount seems to be given off very slowly:

I. 0.4050 gram of the air-dried salt lost *in vacuo* 0.0114 gram of water.

II. 0.2991 gram of the air-dried salt lost *in vacuo* 0.0088 gram of water.

	Calculated for $(C_6H_2C_6H_5NH(NO_2)_2COO)_2Ca.7H2O$.	Found. I.	 II.
$2H_2O$	2.55	2.81	2.94

The salt resembles the sodium salt except that the reddish-orange needles which it forms are shorter. It is readily soluble in water.

A solution of the sodium salt gave the following precipitates with salts of the common metals:

Argentic nitrate gave a precipitate of reddish-orange needles insoluble in cold or hot water.

Cupric sulphate gave a yellow precipitate, insoluble in cold water, slightly soluble in hot.

Ferric chloride or *manganous chloride* gave a precipitate consisting of orange needles slightly soluble in cold water, moderately soluble in hot.

Nickelous chloride gave a yellow precipitate, moderately soluble in cold, freely soluble in hot water.

Cadmic sulphate, *zincic sulphate*, *baric chloride*, or *strontic chloride* gave an orange precipitate, moderately soluble in cold, readily soluble in hot water.

Magnesic sulphate gave no precipitate, but, on standing, a large number of red needles arranged in radiating groups were deposited, which were readily soluble even in cold water.

Anilidodinitrobenzoic Ethyl Ester, $C_6H_2C_6H_5NH(NO_2)_2COOC_2H_5$.—The acid mixed with an amount of absolute alcohol, in which it only partially dissolved, was saturated with dry hydrochloric acid gas, and then heated for a short time on the steam-bath. The liquid was then allowed to cool, and the undissolved portion filtered out. This proved to be nearly pure ester, and was easily purified by crystallization from alcohol. An additional amount of the ester was obtained by diluting the filtrate, and purified by crystallization from a mixture of benzol and alcohol. The pure ester showed the constant melting-point, 154°. It was dried and analyzed with the following result:

0.1926 gram of the substance gave, on combustion, 0.3842 gram of carbonic dioxide and 0.0700 gram of water.

	Calculated for $C_6H_2C_6H_5NH(NO_2)_2COOC_2H_5$.	Found.
Carbon	54.39	54.40
Hydrogen	3.93	4.04

Two grams of anilidodinitrobenzoic acid gave 2.1 grams of the ester instead of the 2.19 grams required by theory; the yield therefore amounted to 96 per cent.

Properties of Anilidodinitrobenzoic Ethyl Ester—It crystallizes from a mixture of benzol and alcohol in thin plates or long prisms, apparently of the monoclinic system and having a bright orange color. It melts at 154°. It is very soluble in chloroform; freely soluble in benzol, or acetone; soluble in ether, carbonic disulphide, glacial acetic acid, or ethyl acetate; slightly soluble in ethyl or methyl alcohol, or ligroïn, its solubility in these solvents being increased somewhat by heat. The best solvent for it is a mixture of benzol and alcohol in the proportion of 1 to 2. Cold dilute acids or alkalies do not dissolve it, but it is saponified by them when hot. Sodic ethylate gives a cherry-red color, but this color is not produced by aqueous sodic hydrate.

Nitrous Acid and Anilidodinitrobenzoic Acid.

In the hope of preparing a nitroso compound, 1 gram of anilidodinitrobenzoic acid dissolved in 25 grams of pure benzol was mixed with 100 cc. of dilute hydrochloric acid, and to the well-cooled mixture small pieces of sodic nitrite were added from time to time, the experiment being carried on in the same way as that for making the corresponding toluol compound. After this treatment had been continued a long time the benzol was evaporated with a stream of air, when the 1 gram of the acid was recovered unaltered. If, therefore, the nitroso compound of the acid can be formed at all, its formation is much more difficult than that of the corresponding toluol compound.

Action of Sodium Malonic Ester on Bromdinitrobenzoic Acid.—Formation of Dinitrocarboxylphenylmalonic Ester,

$$C_6H_2CH(COOC_2H_5)_2(NO_2)_2COOH.$$

Five grams of bromdinitrobenzoic acid dissolved in about 30 cc. of absolute alcohol were treated with 5 grams of malonic ester previously converted into the sodium compound by the addition of an alcoholic solution of the sodic ethylate made from 1.5 grams of sodium. This gives the proportion of a little less than 2 molecules of malonic ester to each molecule of the bromdinitrobenzoic acid. A strong dark-red color appeared as soon as the substances were mixed, but to be certain that the reaction was complete, the mixture was allowed to stand at the ordinary temperature over night. Under these conditions a precipitate was formed consisting partly of sodic bromide, and partly of bunches of red crystals of the sodium salt of the new compound. Disregarding this precipitate, water and dilute sulphuric acid were added, which decolorized the solution, and precipitated a yellowish oil. This was separated from the aqueous liquid and allowed to stand, when it solidified in a short time, and was then purified by crystallization from alcohol until it showed the constant melting-point, 176°, when it was dried at 100°, and analyzed with the following results:

I. 0.2282 gram of the substance gave, on combustion, 0.3783 gram carbonic dioxide and 0.0960 gram of water.

II. 0.2237 gram of the substance gave 15.8 cc. of nitrogen at a temperature of 25°.5 and a pressure of 765 mm.

	Calculated for	Found.	
	$C_6H_2CH(COOC_2H_5)_2(NO_2)_2COOH$.	I.	II.
Carbon	45.40	45.23	....
Hydrogen	3.78	4.67	....
Nitrogen	7.57	....	7.88

Five grams of the bromdinitrobenzoic acid gave 4.5 grams of the carboxyldinitrophenylmalonic ester instead of the 6.4 grams calculated from the formulas, that is, a yield of 70 per cent.

The formation of this substance from the bromdinitrobenzoic acid takes place with great ease, as it was found that a mixture of the brom acid, malonic ester, and alcohol, if treated with dilute aqueous sodic hydrate, was at once colored deep red by the formation of the sodium salt of the carboxydinitrophenylmalonic ester, and upon acidifying this red solution with dilute sulphuric acid a precipitate of the free ester was obtained, while sodic bromide could be detected in the filtrate. In none of this work was any dinitrobenzoic acid detected, which might have been formed by the replacement of the bromine by hydrogen, as happens in the corresponding reaction with tribromdinitrobenzol.

Properties of Carboxydinitrophenylmalonic Ester, $C_6H_2CH(COOC_2H_5)_2(NO_2)_2COOH$.—It crystallizes from alcohol in short, thick, white prisms terminated by a plane at an oblique angle. It melts at 176°. It is very soluble in acetone; readily soluble in ethyl acetate; moderately soluble in cold ethyl or methyl alcohol, ether, or glacial acetic acid, readily soluble in each of these liquids if hot; moderately soluble in benzol, chloroform, or carbonic disulphide; essentially insoluble in water or in cold ligroïn, and slightly soluble in hot ligroïn. The best solvent for it is alcohol. Dilute acids in the cold have no effect upon it. It dissolves in aqueous solutions of the alkalies or alkaline carbonates forming the dark-red salts. It behaves like a dibasic acid.

Silver Ammonium Salt of Carboxydinitrophenylmalonic Ester.—A weighed amount of the carboxydinitrophenylmalonic ester was dissolved in water which contained 2 molecules of ammonic hydrate for each molecule of the ester, and, after filtering, a solution of argentic nitrate was added to it slowly with constant stirring. A precipitate was formed at once, and, after an excess of argentic nitrate had been added, and the whole thoroughly stirred, the red color of the ammonium salt almost entirely disappeared. The heavy, white precipitate was filtered out and thoroughly washed with water, although it dissolved in it to an appreciable extent. The salt was dried in the air, as it was found to be decomposed if heated to 100°, forming at first a reddish and afterward a black amorphous mass. This precipitated salt was used in Analyses II. and III. In one preparation the wash waters were allowed to run into the filtrate, which contained a large excess of argentic nitrate. On standing over night white crystals were deposited, which were filtered out, washed, and dried at ordinary temperatures. They proved identical with the salt formed by direct precipitation, as shown by the following analyses, since in I. these crystals were used:

I. 0.1114 gram of the crystallized salt gave, by heating with nitric acid and a crystal of potassic bromide in a sealed tube, 0.0426 gram of argentic bromide.

II. 0.1213 gram of the precipitated salt gave 0.0463 gram of argentic bromide.

III. 0.1006 gram of the precipitated salt gave 0.0383 gram of argentic bromide.

	Calculated for $C_6H_2CAg(COOC_2H_5)_2(NO_2)_2COONH_4$.	Found. I.	II.	III.
Silver	21.86	21.97	21.93	21.87

These analyses indicate that the salt is an ammonio-silver salt, instead of the disilver salt which we had expected. The relative position of the silver and ammonium in the molecule was not determined. We have put the silver provisionally in the malonic ester group in the formula given above, because the salt is white, whereas the ammonium compound from which it is formed is red, and in other cases we have found that the presence of a basic radical, such as sodium or ammonium, in this group gives rise to red salts; it seems more probable, therefore, that the ammonium has replaced hydrogen in the carboxyl rather than in the malonic ester group.

The salt forms a heavy, white precipitate or white crystals; it is slightly soluble in water and decomposed by heating it to 100°.

Action of Metaphenylene Diamine on Parabromdimetanitrotoluol. Formation of Metamidophenylenimidodinitrotoluol,

$$NH_2C_6H_4NHC_6H_2(NO_2)_2CH_3.$$

This work was undertaken in the hope of obtaining molecules consisting of long chains of phenyl and phenylene rings in order to study the effect of the increasing complexity of the molecules upon the properties of the substances. As explained in the introduction we were unable to carry out our plan, but give here the description of the preparation and properties of the new compounds obtained.

Metaphenylenediamine acts on bromdinitrotoluol with such violence, that, if the substances are mixed without a diluent, enough heat is given off to volatilize a large part of the metaphenylenediamine in dense white clouds, while there is left a black, amorphous, charred mass from which only a very small amount of substance can be extracted. We accordingly mixed the two substances with about three times their volume of alcohol, and, after warming gently for a short time, allowed the alcohol to evaporate spontaneously. The residue was then dissolved in hot hydrochloric acid, and after filtration rendered alkaline with sodic carbonate. This threw down a red precipitate, almost insoluble in water, which was filtered out, washed, dried, and purified by crystallization from a mixture of benzol and alcohol, until it showed the constant melting-point, 185°, when it was dried at 100°, and analyzed with the following results:

I. 0.2039 gram of the substance gave 36.1 cc. of nitrogen at a temperature of 22° and a pressure of 758 mm.

II. 0.1997 gram of the substance gave 33.3 cc. of nitrogen at a temperature of 15° and a pressure of 763 mm.

	Calculated for $NH_2C_6H_4NHC_6H_2(NO_2)_2CH_3$.	Found. I.	II.
Nitrogen	19.45	19.92	19.56

Only 1 molecule of the bromdinitrotoluol therefore had reacted with the phenylenediamine.

Properties of Amidophenylenimidodinitrotoluol ($CH_3$1.$NO_2$3.NH4.$NO_2$5).—Crystallized from benzol and alcohol it forms rather stout, blunt prisms arranged in fan-shaped groups. These prisms are a vivid reddish-brown with a very marked, yellowish-green reflex. From benzol alone it crystallizes in dark red lancet-shaped blades. It melts at 185°. It is very soluble in acetone; freely soluble in methyl alcohol, benzol, chloroform, glacial acetic acid, or ethyl acetate; moderately soluble in ether, carbonic disulphide, or cold ethyl alcohol; more soluble in hot alcohol; almost insoluble in ligroïn or water. The best solvent for it is a mixture of alcohol and benzol. Hydrochloric acid or sulphuric acid forms with it a dark oily mass, probably a salt, as it dissolves in a large quantity of water, and solutions of the alkalies or alkaline carbonates precipitate the unaltered substance from this solution. Nitric acid of specific gravity 1.36 dissolves it forming a yellow solution, from which water precipitates a new yellow body, probably a nitro compound. Cold solutions of alkalies or alkaline carbonates have no action on it, but alkaline solutions when hot decompose it. Sodic ethylate gives with it a green color, very similar to that obtained from anilidodinitrotoluol. It was not converted into an acetyl compound even by boiling for three hours with glacial acetic acid, the original substance being recovered unaltered.

An attempt was made to obtain a reaction between amidophenylenimidodinitrotoluol and bromdinitrotoluol. For this purpose the two substances were mixed in the proportion of equal molecules, heated until they melted, and kept at this temperature for several minutes. No evolution of hydrobromic acid was observed, and on treating the cold mass with water no hydrobromic acid could be detected in the aqueous extract. The product was dissolved in alcohol, and the solution allowed to evaporate spontaneously, when the red lancet-shaped crystals of the amidophenylenimidodinitrotoluol were observed side by side with the slender white needles of the bromdinitrotoluol. It seems, therefore, that the two bodies do not react on each other, and that only one of the amido groups of the metaphenylenediamine can be affected by bromdinitrotoluol.

Many attempts were made to replace the amido group in amidophenylenimidodinitrotoluol with bromine by means of the diazo reaction, but none of them were successful, black, tarry masses being obtained in each case. The experiment was tried with strong hydrobromic acid and an excess of sodic nitrite; with just the calculated amount of sodic nitrite to form the diazo compound, as we thought the bad result might be due to the formation and decomposition of a nitroso compound from the imido group; in acetic acid solution; by Sandmeyer's reaction; and finally an attempt was made to prepare the diazo perbromide, but the bromine instead acted on the phenylene ring forming a tribrom compound.

Tribromamidophenylenimidodinitrotoluol,

$NH_2C_6HBr_3NHC_6H_2(NO_2)_2CH_3$.

This substance was prepared by treating amidophenylenimidodinitrotoluol with bromine water, which converted it into a yellow substance. When the red color of the original body was entirely changed to yellow, the product was filtered out, and purified by crystallization from boiling benzol, until it showed the constant melting-point 222°, when it was dried at 100°, and analyzed with the following result:

0.1445 gram of the substance gave by the method of Carius 0.1552 gram of argentic bromide.

	Calculated for $NH_2C_6HBr_3NHC_6H_2(NO_2)_2CH_3$.	Found.
Bromine	45.71	45.70

The amidophenylenimidodinitrotoluol has therefore taken up three atoms of bromine in place of three of hydrogen, and it is probable that these atoms of bromine are attached to the benzol ring of the amidophenylenimido group. One gram of the original substance gave 1.8 grams of the tribrom compound instead o; the 1.82 grams required by theory. The yield is, therefore, 99 per cent.

Properties of Tribromamidophenylenimidodinitrotoluol.—The substance crystallizes from boiling benzol in rhombic plates of a brownish-yellow color, which melt at 222°. It is easily soluble in acetone; moderately soluble in benzol, chloroform, carbonic disulphide, or ethyl acetate; slightly soluble in methyl alcohol, ether, or glacial acetic acid; almost insoluble in ethyl alcohol, or ligroïn; insoluble in water. Boiling benzol is the best solvent for it. It is slightly soluble in strong hydrochloric acid or nitric acid; fuming nitric acid dissolves it more easily, and water precipitates from this solution a light yellow substance, perhaps a nitro-compound; it is soluble in strong sulphuric acid. Solutions of alkalies produce no effect on it in the cold. When warmed with alkalies, a reaction takes place producing a black solution, from which we did not succeed in isolating a pure substance. We had hoped by this decomposition of the body to determine the position of the atoms of bromine, but, as one of the products of the reaction was bromide of sodium, this was impossible. Sodic ethylate gives a bluish-violet color with it. Aniline had no effect upon it.

Tribromanilidodinitrotoluol, $C_6H_2Br_3NHC_6H_2(NO_2)_2CH_3$.

This substance was prepared in the course of the work on complex molecules mentioned in the introduction to this paper. Bromine water does not act easily upon the anilidodinitrotoluol, which, in this respect, differs from the corresponding amidophenylenimido body, whose behavior was described above. It was necessary, therefore, to use pure bromine, some of which was poured into an evaporating dish, and anilidodinitrotoluol added in small amounts at a time. The action was violent, the substance dissolving, and fumes of hydrobromic acid being given off. Enough bromine should be taken to moisten thoroughly all the solid used. The excess of bromine was evaporated off, the solid residue broken up and washed with cold alcohol, in which it is almost insoluble. The yellow powder thus obtained was recrystallized from boiling benzol until it showed the constant melting-point, 238°, when it was dried at 100°, and analyzed with the following result:

0.1918 gram of the substance gave, by the method of Carius, 0.2107 gram of argentic bromide.

	Calculated for $C_6H_2Br_3NHC_6H_2(NO_2)_2CH_3$.	Found.
Bromine	47.05	46.75

Properties of Tribromanilidodinitrotoluol.—It crystallizes from boiling benzol in yellow rhombic plates often with the acute angles truncated, which melt at 238°. It is soluble in chloroform or carbonic disulphide; moderately soluble in benzol, acetone, or ethyl acetate; slightly soluble in ether or glacial acetic acid; almost insoluble in ethyl or methyl alcohol, or in ligroïn; insoluble in water. Benzol is the best solvent for it. It is insoluble in either of the three strong acids, but dissolves in fuming nitric acid. A solution of sodic hydrate has no action on the substance, even if boiled with it for several minutes.

In the course of the work on complex molecules outlined in the introduction, an attempt was made to convert the substance just described into a nitro compound. For this purpose the tribromanilidodinitrotoluol was mixed with nitric acid of specific gravity 1.5, in which it dissolved without evolution of nitrous fumes forming a red solution. Cold water separated from this solution a precipitate resembling red sulphide of antimony in appearance, which was washed with water and dried. All our attempts to obtain a crystalline body from this precipitate have failed. It dissolved in several of the organic solvents, but these solutions left on evaporation a red viscous or resinous substance, which showed no signs of crystallization, even after long standing.

We next heated this product with aniline in the hope of getting a more manageable anilido compound. An anilido compound was produced, as shown by the formation of aniline bromide, and this proved that the uncrystallizable substance was a nitro compound, since the tribromanilidodinitrotoluol, from which it was made, did not give up bromine to aniline. This new anilido compound, however, behaved with solvents in the same unsatisfactory manner as the nitro compound, from which it was derived. Nor did a bromine derivative which was formed from this new anilido compound by the action of bromine, as indicated by the evolution of hydrobromic acid, show any signs of crystallization. As none of these derivatives could be brought into a state fit for analysis, we were obliged to give up this branch of the work.

Action of Pyridine on Bromdinitrobenzoic Acid.

If bromdinitrobenzoic acid is added to pyridine it gives a white crystalline precipitate, which almost immediately dissolves with evolution of heat, and from this new solution a heavy yellow precipitate is thrown down. To isolate the two products, which seemed to be formed by this action, we dissolved some bromdinitrobenzoic acid in absolute alcohol, and added to it an excess of pyridine, when white needles separated in large quantity. These were filtered out, washed with absolute alcohol, in which they were not very soluble, and then analyzed, but the result obtained did not correspond to any formula. It seemed to indicate rather that the substance was a mixture of the pyridine salt of bromdinitrobenzoic acid and the free acid ; and this, as a matter of fact, is what we should have obtained, if the original crystals had been this pyridine salt, as they lost pyridine with great ease, when treated with alcohol. Although the analysis did not settle the composition of the crystals, the following facts leave little doubt that they were the salt

$$C_6H_2Br(NO_2)_2COOHC_5H_5N.$$

They showed the solubility of a salt, being slightly soluble in cold and freely soluble in hot water; sodic hydrate set free pyridine, and acids precipitated bromdinitrobenzoic acid from a solution of them. The solution gave no test for a bromide. Sodic ethylate gave the same reddish-purple color, which it gives with salts of bromdinitrobenzoic acid. We may add that the crystals were moderately soluble in cold, easily soluble in hot alcohol, and that with an excess of pyridine they passed easily into the yellow product obtained direct from pyridine and the acid.

The yellow product was prepared by evaporating the mother-liquor from the white salt, which still contained some of the crystals, or even by allowing it to stand at ordinary temperatures. We did not attempt to analyze this substance, as it is decomposed even by crystallization from alcohol, but we have been able to draw a safe inference in regard to its nature from its decomposition-products and its properties. As first prepared, it melted with decomposition at about 210°, but, if it was recrystallized from alcohol, some bromide of pyridine was eliminated, and the crystals showed a higher melting-point. By continuing the crystallization often enough all the bromine and pyridine were removed as bromide of pyridine, and the crystals melted constant at 245°–246°, and contained no bromine. This same substance could be obtained from the yellow substance by treating it with dilute sulphuric acid. After recrystallization from alcohol it appeared in elongated hexagonal plates of a light straw color. To determine the nature of this substance, it was converted into its calcium salt by warming it with calcic carbonate and water. The solution thus obtained was filtered, and upon concentration deposited yellowish-orange, well defined octahedra of the salt, which, after it had been crystallized, redissolved with great difficulty. The crystals were filtered out, pressed between filter paper, dried in the air, and analyzed with the results given under I. The filtrate, on further concentration, gave another crop of crystals, which were dried in the same way, and analyzed with the results given under II. The mother-liquor from these second crystals, when acidified, gave the acid with its proper melting-point, 245°–246°.

I. 0.2552 gram of the air-dried salt lost 0.0304 gram of water when heated to 157°.

II. 0.5226 gram of the air-dried salt lost 0.0602 gram of water at 160°.

	Calculated for $CaOCOOC_6H_2(NO_2)_2.2H_2O$.	Found. I.	II.
Water	11.92	11.92	11.52.

I. 0.2248 gram of the salt dried at 157° gave 0.1122 gram of calcic sulphate.

II. 0.4624 gram of the salt dried at 160° gave 0.2269 gram of calcic sulphate.

	Calculated for $CaOCOOC_6H_2(NO_2)_2$.	Found. I.	II.
Calcium	15.04	14.69	14.44

These results leave no doubt that the substance is the calcium salt of oxydinitrobenzoic acid, but the melting-point of this acid, 245°–246°, did not agree with that given by H. Salkowski[1] for paroxydimetanitrobenzoic acid which was 235°–237°. We accordingly made a careful study of the melting-point of this acid, which is described in a later section, and proved that its true melting-point is 245°–246°.

The work just described shows that the yellow pyridine compound is broken up by crystallization from alcohol, or by dilute sulphuric acid, into oxydinitrobenzoic acid and bromide of pyridine. That it was not a mixture of these two substances was shown by the fact that it took several crystallizations to remove all the pyridine and bromine, whereas bromide of pyridine is so soluble in alcohol that the whole of it would have been removed by the first crystallization, if it had existed already formed. That the substance is a salt is made probable by its solubilities, as it is slightly soluble in cold, freely soluble in hot water ; slightly soluble in cold, moderately soluble in hot alcohol ; insoluble in benzol or ether ; and this view is confirmed by the facts that alkalies set free pyridine from its solutions, and argentic nitrate forms a red salt when added to the neutral solution. With an acidified solution it gives a precipitate of argentic bromide, but this may come from the bromide of pyridine formed by the acid, rather than from the original yellow substance. The only formula which we have found that explains all these observations is

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[1] Ann. Chem. (Liebig), **163**, 36.

$$C_5H_5NBrC_6H_2(NO_2)_2COOHC_5H_5N,$$

derived from two molecules of pyridine and one of the bromdinitrobenzoic acid. On this theory one of the molecules of pyridine is attached to the carboxyl group, while the other is attached to the bromine atom and the benzol ring of the substituted benzoic acid, forming a salt analogous to bromide of pyridine, as shown by the following formulas:

$$(C_5H_5N)Br(C_6H_2(NO_2)_2COOHC_5H_5N). \quad (C_5H_5N)BrH.$$

The decomposition of the yellow substance would then be represented by the following reaction:

$$C_5H_5NBrC_6H_2(NO_2)_2COOHC_5H_5N + H_2O = C_5H_5NBrH + HOC_6H_2(NO_2)_2COOH + C_5H_5N.$$

The Melting-Point of Paroxydimetanitrobenzoic Acid.—The acid obtained from the yellow pyridine compound by the action of dilute sulphuric acid or by crystallizing it from alcohol, as described in the preceding paragraph, melted at 245°–246°, which was also the melting-point of the oxydinitrobenzoic acid prepared by us by the action of sodic hydrate on bromdinitrobenzoic acid. All these acids must be paroxydimetanitrobenzoic acid, and, as H. Salkowski[1] ascribes the lower melting-point, 235°–237°, to this body, we have felt it necessary to prepare this acid by the two methods given by him in order to remove this discrepancy. Accordingly, some chrysanisic acid was made by the method of Frederici,[2] the oxidation of dinitrotoluidine melting at 166°, with potassic dichromate and sulphuric acid. This melted at 259°. It was treated with sodic nitrite in a boiling, weak acid solution, until all the chrysanisic acid had been transformed into the new body. This took place very slowly. The product melted at the temperature stated by Salkowski, 235°–237°, with decomposition and blackening, but, after repeated crystallization from alcohol, the melting-point rose to 245°, and the signs of decomposition during melting vanished.

In order to apply Salkowski's second method some chrysanisic acid was heated with a dilute solution of sodic hydrate.

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[1] Ann. Chem. (Liebig), **163**, 36.

[2] Ber. d. chem. Ges., **11**, 1975.

The mixture became dark-colored, and ammonia was given off. The liquid was evaporated to dryness on the steam-bath, the residue taken up with a little hot water, filtered, and precipitated with hydrochloric acid ; this yielded a crude product, melting a little above 240°, which was raised to the constant melting-point, 245°, by crystallization from alcohol. If the heating of the chrysanisic acid was continued for a long time with a strong alkaline solution, upon acidification of the liquid no oxydinitrobenzoic acid was deposited, but there was a vigorous evolution of hydrocyanic acid. This behavior is analogous to that of the anilidodinitrobenzoic acid described earlier, which gives aniline and oxydinitrobenzoic acid at first with sodic hydrate, but by more vigorous treatment phenyl isocyanide. It also recalls the work of Wöhler[1] and of Post and Hübner[2] on the formation of cyanides by the action of alkaline hydrates in aqueous solution on aromatic nitro compounds.

The work just described shows that paroxydimetanitrobenzoic acid prepared in four different ways had the constant melting-point 245°–246°, and, therefore, that the melting-point 235°–237° ascribed to it by H. Salkowski rests probably on an error of observation. We should add that the thermometer used in this work was tested by determining the boiling-point of aniline and naphthalene with it. Aniline with the column in the vapor and at a pressure of 760 mm. showed the boiling-point 184°. Naphthalene under the same conditions gave a temperature of 218°–219°. There can be no doubt, therefore, that the thermometer was accurate enough for this work.

Chlordinitrobenzoic Acid.

The following work on the chlor compound could not be finished so thoroughly as we wished, because of the pressure of other parts of the research, but we have decided to describe our observations even in this imperfect state, since they seem to leave no doubt in regard to the nature of the substance obtained.

A quantity of chrysanisic acid was mixed with cold, strong hydrochloric acid, and treated with an excess of sodic nitrite.

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[1] Pogg. Ann. **13**, 488, (1828).

[2] Ber. d. chem. Ges., **5**, 408, (1872).

To the mixture was then added a solution of cuprous chloride in strong hydrochloric acid, and the whole heated for about half an hour with occasional addition of more sodic nitrite. After the liquid had been cooled by the addition of water the product, a reddish, viscous mass, was removed by winding it about a rod, and was then sucked out as completely as possible with a filter pump. The residue was pressed between filter paper, and recrystallized from alcohol, and later from benzol, which is much more efficient in removing the tarry matter. In this way a crystalline body was obtained, the melting-point of which we did not succeed in raising above 159°, but we do not feel certain that the true melting-point may not lie a few degrees above this temperature, as our work was done with an insufficient amount of material, the yield being exceedingly small. For this reason also we were unable to analyze the substance, but the following observations show without doubt that it is chlordinitrobenzoic acid. It is insoluble in water or acids, but dissolves easily in alkalies or alkaline carbonates. It dissolves in aniline with the aid of heat, forming aniline chloride, and an orange-red acid, melting when not perfectly pure at 235°–238°; anilidodinitrobenzoic acid melts at 239°. This product also gave the pansy-purple color with sodic ethylate, which is characteristic of anilidodinitrobenzoic acid, whereas the chlor acid, melting at 159°, gives with sodic ethylate a reddish-purple color, closely resembling that obtained from bromdinitrobenzoic acid. With ammonic hydrate the acid, melting at 159°, gave ammonic chloride and a substance resembling chrysanisic acid in appearance, and melting in the crude state not far from the melting-point of this acid.

Properties of Chlordinitrobenzoic Acid.—It crystallizes in white, rather ill-defined, prisms, which probably melt at 159°. It is very soluble in ether or acetone; easily soluble in methyl alcohol, glacial acetic acid, or ethyl acetate; moderately soluble in ethyl alcohol, benzol, chloroform, or carbonic disulphide; almost insoluble in ligroïn. Benzol is the best solvent for it.

Action of Hydrochloric Acid on Bromdinitrobenzoic Acid.

These experiments, like those described in the preceding section, are unfinished, as it was intended to make this work the starting-point for a new research and, therefore, the study of the most interesting product of the reaction has been postponed until that could be undertaken. Bromdinitrobenzoic acid in quantities of two grams at a time was heated with fifteen cc. of hydrochloric acid, containing 11 per cent. of the acid, to 200° for five hours in a sealed tube. At the end of this time, it was found that the undissolved portion had collected into a liquid globule. The whole contents of the tube were poured into an evaporating dish, and allowed to stand, until the globule had solidified, and crystals had separated from the supernatant liquid. As these crystals gave with sodic ethylate the characteristic reddish-purple color of bromdinitrobenzoic acid, they were heated with a dilute solution of sodic carbonate on the steam-bath until no more dissolved. The residue melted after one recrystallization from alcohol at 119°, and was probably vicinal bromdinitrobenzol, although this supposition needs confirmation by analysis before it is accepted. The dark-red solution obtained by sodic carbonate gave, when acidified, a precipitate, which, by crystallization from alcohol, was separated into two substances. One of these melted at 245°, and was, therefore, oxydinitrobenzoic acid, formed by the action of the solution of sodic carbonate upon the bromdinitrobenzoic acid, although possibly some of it was one of the direct products of the reaction. The other substance melted at 62°, and we, therefore, inferred that it was the vicinal dinitrophenol ($OH.1.NO_2.2.NO_2.6.$) as this melts at 61°.78 according to Mills,[1] whereas its melting-point is given usually as 63°–64°. To confirm this view, we oxidized the substance with nitric acid, which converted it into picric acid, recognized by its melting-point 121°, its copper and lead salts, and the deep red color produced when it was heated with potassic cyanide. The formation of the dinitrophenol was to be expected, as Salkowski and Rudolph[2] have found that oxydinitrobenzoic acid, if heated with water to

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[1] Phil. Mag. [5], **14**, 27.

[2] Ber. d. chem. Ges., **10**, 1255.

170° is converted into this vicinal dinitrophenol. The products of the action of hydrochloric acid at 200° on bromdinitrobenzoic acid would seem to be the following: Bromdinitrobenzol (?) ($Br.1.NO_2.2.NO_2.6.$) about one-fourth of the product; dinitrophenol of the same series, about one-third of the remainder; and unaltered bromdinitrobenzoic acid mixed perhaps with some oxydinitrobenzoic acid.

ALUMINUM ETHYLATE.[1]

BY H. W. HILLYER AND O. E. CROOKER.

In our preliminary notice, which appeared in this JOURNAL under the head of "Aluminum Alcoholates,"[2] mention was made of our investigation, as then incomplete, of the action of alcoholic solutions of anhydrous chlorides upon aluminum. That part of the work wherein ethyl alcohol was used has been completed, and the results as obtained are given in this article.

In their work on aluminum alcohols,[3] Gladstone and Tribe have prepared, by means of their aluminum-iodine reaction, several aluminum alcoholates, among which was the ethylate. Their method of procedure was as follows: by bringing together 2 grams of aluminum foil, 1 gram of iodine, and 20 cc. of absolute alcohol the elements were found to combine quickly and to produce the aluminum iodide necessary for the reaction, whereupon the decomposition of the alcohol began before the whole of the free iodine had passed into combination. The action proceeded with moderate rapidity until the metal had disappeared and the evolution of hydrogen ceased. The reaction was supposed to take place through the intervention of intermediate bodies, as follows:

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[1] After sending this article to the editor, our attention was first directed to a note by Mr. W. Tistschenko, in the October Journal. Although in many respects our results are identical with his, it still seems to us desirable to publish them, since our method is not the same, and since related facts not hinted at in the note above mentioned have been observed in the course of our research. It is our purpose to complete the work already begun with methyl and the two propyl alcohols.

[2] This JOURNAL, **18**, 621.

[3] J. Chem. Soc., 1881, **39**, 1; 1882, **41**, 5; 1886, **49**, 25.

(*a*) $3C_2H_5OH + Al_2I_6 = Al_2(C_2H_5O)_3I_3 + 3HI$;
(*b*) $Al_2(C_2H_5O)_3I_3 + 3C_2H_5OH = Al_2(C_2H_5O)_6 + 3HI$;
(*c*) $6HI + Al_2 = Al_2I_6 + 3H_2$.

The contents of their flask was then heated in an oil-bath to about 300°, and held at this temperature until the excess of alcohol had been driven off.

The residue in their flask was next distilled under diminished pressure[1] and a yellowish white distillate obtained which melted at 115° C.,[2] and boiled somewhere near the limits of the ordinary mercurial thermometer. This substance, to which they gave the name aluminum ethylate, was found to be quite free from iodine, and to contain considerable aluminum. It dissolved slightly in absolute alcohol, and from alcoholic solution water precipitated aluminum hydroxide. Heat at atmospheric pressure decomposed it into aluminum oxide, alcohol, ethylene, and ether.

Even though distilled *in vacuo*, they found considerable decomposition taking place, and on analysis it was usually found that there was from 1 to 2 per cent. of aluminum present in excess of that which the ethylate would require.

Wislicenus and Kaufmann observed in their recent work on amalgamated aluminum[3] that when they used it for the reduction of nitrobenzene, amyl nitrite, and similar substances in absolute alcoholic solution, a violent reaction took place, and a semi-solid mass was formed which they supposed to be a mixture of aluminum hydroxide and aluminum ethylate, but from which it was impossible to isolate any of the latter substance by distillation *in vacuo* according to the method of Gladstone and Tribe. The aluminum, however, had apparently gone into combination with the alcohol, and upon addition of water to the mixture separated out as the hydroxide.

In work with amalgamated aluminum prepared after the method of Wislicenus and Kaufmann[4] for the purpose of reduction in neutral solutions, a reaction was observed which led to an investigation—one part of which we have just completed, but which we began before the second article of Wislicenus and Kaufmann came to our notice.

[1] J. Chem. Soc., 1876, **29**, 161.

[2] Given by them in a later article as 130° C.

[3] Ber. d. chem. Ges., **28**, 1985.

[4] Ber. d. chem. Ges., **28**, 1323.

Aluminum in the form of fine chips cut from the block by means of a milling machine was amalgamated according to their method of first etching it with caustic soda, washing with water to remove the alkali, and then treating with an aqueous solution of mercuric chloride until strong evolution of hydrogen began. According to the authors, the amalgam thus prepared could be kept ready for use under dehydrated petroleum ether after first washing with alcohol and ether to remove any remaining traces of water. We experienced considerable difficulty, however, in obtaining an amalgam which had not become somewhat deteriorated by the necessary exposure to the air in preparation. To overcome this difficulty it occurred to us that we might bring about the amalgamation without contact with the air, or of moisture of any kind, by using a solution of mercuric chloride in absolute alcohol. We should then be able to use the amalgam in this solution for neutral reductions by simply adding water for the amalgam to act upon.

A solution of mercuric chloride in ordinary absolute alcohol was first used, and an evolution of gas observed. Thinking this to be due to the presence of moisture, we distilled some absolute alcohol which had been subjected to the action of our amalgam for some time, and found even with this alcohol, which could scarcely contain any water, that we had a reaction which was as violent, if not more so, than the action of the amalgam on water itself. It was further observed that the action continued with constant evolution of gas, and considerable rise in temperature, until the contents of our flask became, first gelatinous, and finally solid.

During the reaction the mercuric chloride became reduced, and considerable metallic mercury was to be seen at the bottom of the flask. On treating with water the substance gave a copious precipitate—apparently aluminum hydroxide—and the odor of alcohol was quite evident. This, together with the reaction itself, suggested that possibly we had aluminum ethylate formed. The reaction seemed to be rather remarkable, however, because, according to Wislicenus and Kaufmann, aluminum amalgam does not decompose absolute alcohol,[1] and also because, according to Gladstone and Tribe, aluminum chloride, which might be formed, gives no reaction even when boiled with absolute alcohol and aluminum.[2] We interpreted it, however, to be due to the joint influence of the aluminum-mercury couple and to the aluminum chloride formed in the reduction of the mercuric chloride.

Knowing from the work of Gladstone and Tribe that aluminum alcoholates, in contrast with all other known alcoholates, can be distilled under diminished pressure, we then attempted to distil the product obtained in our first reaction. Distillation was begun under a pressure of 20 mm. On applying heat the substance melted, white fumes being given off, and upon heating to the boiling-point, a transparent liquid passed over. This became grayish white as it cooled in the receiver, and was found to contain aluminum and some mercury. It had the consistency of beeswax, and possessed a very peculiar, though not disagreeable odor. The residue in the retort was of a varnish-like appearance, insoluble in the ordinary solvents. It still contained unchanged aluminum.

The distillate, which we supposed to be aluminum ethylate, was found to decompose with extreme rapidity when in contact with the moisture in the air, and also when heated at the atmospheric pressure.

In order to avoid the use of mercury, which not only caused trouble on distillation due to "bumping," but also passed over and contaminated the distillate, we made experiments with other anhydrous chlorides in the hope of finding a method of overcoming this difficulty.

Platinic chloride dissolved in the same manner in absolute alcohol gave, with chipped aluminum, an evolution of gas, but the action was not as violent nor of as long duration as with mercuric chloride. The platinic chloride was broken up like the mercuric chloride, metallic platinum being deposited on the walls of the flask. Fuming stannic chloride was next tried, and a very violent reaction resulted, hydrogen being rapidly evolved, and spongy tin being deposited on the aluminum.

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[1] Ber. d. chem. Ges., **28**, 1324,

[2] J. Chem. Soc., 1876, **29**, 162.

An experiment was then carried out with stannic chloride. 5 grams of chipped aluminum, and 1 cc. of fuming stannic chloride in 50 cc. of absolute alcohol were used. The action began at once and was accompanied by a considerable rise in temperature. It continued at the temperature of the laboratory for three or four days, when the contents of the flask had become quite solid. This was then distilled as before, and all precautions were taken to obtain the substance in as pure condition as possible. Distillation was begun at a pressure of 23 mm. Gentle heat was applied until the contents of the distilling flask had reached almost the boiling-point, and continued for some time until all of the white fumes had passed over. A distilling flask was then placed in position as a receiver, and as much of the substance as would distil without decomposition was allowed to pass into it. This flask was then disconnected, provided with a thermometer, and the contents fractionated under diminished pressure with an apparatus resembling that used by Brühl for fractionation *in vacuo*, but modified slightly to enable us to heat the receiver quite hot in an air-bath.

The substance boiled evenly during the distillation, and the thermometer rose slowly from 235° C., as the first portion began to come over, to 245° C., when the distillation was complete. Our distillate, which we collected in three portions, was a clear transparent liquid which, on cooling, became white and opaque, owing to an apparent tendency to crystallize, but still of a gummy consistency. It melted at 135° C. and boiled constantly, within the above-mentioned range, at a pressure of 23 mm. It was only very slightly soluble in absolute alcohol, but more so in ether and benzene. Chloroform did not dissolve it. That obtained in this experiment possessed the same peculiar odor as had been noticed before. The middle portion was analyzed for aluminum. The average of six determinations by ignition, after treating with nitric acid, resulted in showing that it contained 18.13 per cent. of aluminum. As this was considerably in excess of the theoretical amount in aluminum ethylate (16.66 per cent.) it was decided that our distillate was either a mixture of aluminum ethylate and aluminum hydroxydiethylate—a substance which we think might easily result from a partial de composition due to presence of moisture in the alcohol—or that it contained an impurity from which, as yet, we had been unable to free it.

A test in our latest distillate showed the presence of chlorine, and we decided, therefore, that the excess of aluminum in our ethylate must be due to the presence of some aluminum chloride, which volatilized at a low heat, and condensed along with our substance in the receiver.

In a later experiment, where we used as high a quantity as 6 cc. of stannic chloride, in order to determine whether the amount of chloride had any influence on the rate of reaction, it was found, on heating to distil, that there was scarcely any substance present which would fuse, and that the white fumes, which had been only moderate in other cases, were now greatly increased, and condensed as a feathery mass in the receiver. This, on analysis, was found to be aluminum chloride.

	Calculated for $AlCl_3$.	Found.
Aluminum	20.22	20.13

A new portion was made up, and distilled several times in order to obtain it free, if possible, from aluminum chloride, but without success.

Determinations were then made of the amount of chlorine and aluminum contained in the same sample, and it was found that, deducting the amount of aluminum which was present as aluminum chloride, there remained an average of 17.71 per cent. of aluminum to be accounted for as the ethylate, and, although this percentage is large, we consider it entirely within the limits of error of analysis, on account of the hygroscopic character of the ethylate.

	Calculated for $Al(C_2H_5O)_3$.	Found. I.	II.
Aluminum	....	18.05	17.76
Chlorine	....	6.15	6.09
Aluminum as ethylate	16.66	17.86	17.57

These analyses show that it corresponds more closely to the ethylate than to any other substance likely to be formed.

Experiments were carried out in order to see whether the amount of stannic chloride used had any effect either upon the rate of reaction or upon the amount of ethylate formed.

Amounts of chloride varying from 1 to 6 cc. were used with the usual amounts of aluminum and alcohol. The results showed that, when large amounts of chloride were used, the contents of the flask became solid much more quickly, but that the mass consisted almost entirely of aluminum chloride which, on heating under diminished pressure, volatilized and condensed as before stated in the receiver. But little ethylate was formed.

The reaction is more successful when small amounts of stannic chloride are used, even though it takes place more slowly.

An effort was made to free the distillate from chlorine by distilling it in presence of lead oxide. This was not successful, however. There was decomposition on heating, and the distillate obtained was still contaminated with chloride.

As to the reactions involved in what we call our aluminum-stannic chloride reaction, we can only say, that we believe it to be due to the joint action of the couple and the aluminum chloride, neither of which alone seems to be capable of bringing it about. The couple prepared by using an alcoholic solution of stannic chloride, and washing to remove all traces of chloride, proved inactive, but, when freshly prepared aluminum chloride, made by the action of hydrochloric acid gas on aluminum, was added, the reaction began at once. Without the tin, however, the chloride had no effect in the presence of aluminum. The increased rapidity of action when increased amounts of stannic chloride are added, may also be attributed to the influence of the greater amounts of aluminum chloride formed in the initial reaction.

The ethylate we have obtained by this reaction shows properties similar to those found by Gladstone and Tribe. In color, however, ours was of a pure white, while theirs is described as yellowish-white. This color, we think, from their reaction might very easily be due to the presence of a slight trace of iodine.

In further work with the alcoholates prepared by means of our aluminum-stannic chloride reaction we hope to throw more light on some of those points which are as yet not quite clear.

ORGANIC CHEMICAL LABORATORY,
UNIVERSITY OF WISCONSIN,
October 12, 1896.

ON THE CONDITIONS AFFECTING THE VOLUMETRIC DETERMINATION OF STARCH BY MEANS OF A SOLUTION OF IODINE.

BY FANNIE T. LITTLETON.

The investigation of which this paper is an account was undertaken at the University of Virginia, under the direction of Dr. J. W. Mallet, for the purpose of ascertaining if a satisfactory process for the volumetric determination of small quantities of starch can be based on the colorimetric use of the so-called iodide of starch.

After the investigation had been completed, an article of 16 pages, summarizing the results of various previous workers, on the various methods of determining starch, appeared in the *Zeitschrift für analytische Chemie* of Fresenius (35ter Jahrg, S. 607). Among the methods mentioned are several based on the use of iodine. The results of many efforts to estimate the amount of iodine held in combination by 1 gram of starch were found to vary so greatly as to warrant the conclusion that a firm union between the two does not exist, but the amount of starch iodide formed is dependent upon the concentration of the solution. A colorimetric determination by means of the iodine reaction is noted, the work being done by M. Dermstedt and F. Voigtländer. The authors recommend the use, as a standard, of a pure starch of the same kind as the one to be estimated, for instance with wheat flour, wheat starch. For accuracy, the average of a great number of estimations is recommended. The authors set forth as the advantages of this method the rapidity and ease with which it may be carried out, and the fact that the result gives starch alone, unmixed with other carbohydrates.

At the beginning of my work a solution of 0.1 gram to the liter, wheat starch being used as the working material, was found to be a convenient strength. Ten cc. of this solution, to which 0.75 cc. of a standard solution of iodine (1 gram to the liter) was added, when diluted to 50 cc., gave a blue color of depth suitable for accurate recognition of differences in intensity.

The standard solution of iodine was made by dissolving iodine in a solution of potassium iodide in the proportion of 1 atom of the former to 1 molecule of the latter—iodine 126.5 to potassium iodide 165.5.

In all the following experiments the starch used was dried to a constant weight.

Using the wheat starch solution above mentioned and the standard iodine solution, the influence of temperature was first examined. It was found that a rise of 5°, or less than this produced no clearly perceptible effect; above this the color of the solution became perceptibly fainter, and almost disappeared when 15° additional had been reached.

The starch dissolving in water alone only after long continued boiling, the effect of the addition of alkali was tried. It was found that as little as 0.002 gram of potassium hydroxide was sufficient to cause 1 gram of starch to dissolve easily, larger quantities having the same result and producing no effect upon the color of the starch iodide solution if the solution was carefully neutralized with acid before the iodine was added.

Solutions of various kinds of starch were then compared. Taking as 100 an exceptionally pure specimen of arrowroot starch (which was used as a standard in all experiments following), by comparing the heights of columns of corresponding color taken from solutions of equal amounts of starch, the strengths, varying inversely as the heights of the columns, were as follows:

Arrowroot	100
Potato	97.06
Wheat	94.81
Tapioca	90.41
Rice	83.83

These results agree with what we should expect, considering the known size of the starch granules. The determination of the amount of true starch by the starch iodide formed, represents only the granulose, since the cellulose or outer covering of the granules gives, in its normal state, no reaction with iodine. Rice starch, having smaller granules and hence a relatively larger surface and probably a proportionally large amount of cellulose, we should not expect to show as great a percentage of true starch as the arrowroot with its larger granules.

Taking a standard starch solution of 0.0001 gram to the cc. and a standard iodine solution of 0.00008 gram to the cc., the relative amounts of starch and iodine necessary to produce the maximum color were found in various cases as follows :

Starch.			Iodine.	
0.007	gram	required	—0.00448	gram.
0.006	"	"	—0.00384	"
0.005	"	"	—0.00320	"
0.004	"	"	—0.00256	"
0.002	"	"	—0.00128	"
0.001	"	"	—0.00064	"

From which it appears that the varying amounts of iodine used are proportional to the amounts of starch.

Taking the same amount of starch, from a solution, 1 cc. of which contains 0.0002 gram, with iodine solutions of different strengths, the maximum color was obtained with the following results :

Starch.											Iodine.	
0.002	gram	with	iodine	solution	of	0.05	gram	to	liter	required	0.00175	gram.
0.002	"	"	"	"	"	0.08	"	"	"	"	0.00128	"
0.002	"	"	"	"	"	0.1	"	"	"	"	0.00128	"
0.002	"	"	"	"	"	0.2	"	"	"	"	0.00160	"
0.002	"	"	"	"	"	0.4	"	"	"	"	0.00120	"

This shows the dissociating effect of the additional water contained in the weaker iodine solutions, also that the conclusion from the first table is only true when a solution of iodine of a single strength is used.

To trace, if possible, some law for the dissociating effect of water, the set of experiments below were made. I took 0.005 gram starch in 20 cc. of water, found the maximum color produced by the addition of 0.002 gram iodine (from a solution 0.2 gram to the liter) and diluted the mixture to 50 cc. I then took a mixture consisting of 95 per cent. of the above amount of starch (the solution being of the same strength) and a proportional amount of iodine from the solution used in the first case. Diluting the mixture to 50 cc. and comparing strengths by the heights of columns of the same depth of color, the apparent amount of starch present was 88.16 per cent. of the standard. In the same way I found the results expressed in the table below, taking in every case the average of four experiments.

Actual amounts of starch. Per cent.	Apparent amounts of starch. Per cent.
100	100.00
95	88.16
90	84.98
85	74.50
80	71.40
75	68.85
70	62.23
65	55.88
60	50.95
55	46.99
50	39.84
45	36.86
40	24.33
35	21.87
30	14.27

Amounts below 30 per cent., when diluted to the standard volume, gave practically no color.

The above table was taken with solutions whose temperatures varied from 33°.6 to 32°.6.

From this it appears that it will be necessary in using the method to compare substances whose percentages of starches do not differ widely.

After the maximum color had been obtained, an additional amount of starch was found to deepen the color until a second maximum was reached, when more starch had no effect. The same result was observed when less than the amount of iodine required for a maximum color was used. This would suggest the inference that the iodine dissociated by water will enter into combination with additional starch. The starch solutions used were more concentrated than those used above, 1 cc. being equivalent to 0.8 milligram.

Finding roughly by use of the iodine reaction that oatmeal contained 38 per cent. of starch, equal volumes of the oatmeal and standard starch solutions were prepared to contain, according to this result, equal amounts of starch. By means of this comparison, however, the oatmeal showed a smaller percentage than that calculated. Concluding this might be due to the presence of albuminoid matter an investigation was made to determine the effect of such matter.

One gram of pure arrowroot starch was dissolved in a liter of water, and, at the same time, another solution in an equal volume of water of 1 gram of a mixture consisting of 50 per cent starch, 10 per cent. cellulose (paper) and 40 per cent. albuminoid matter (white of egg). These solutions were compared, but the amounts of starch, instead of standing as 2 to 1 appeared as 8 to 1. The mixture behaved as if it had 0.25 the amount of starch which had been used in making it. The color also was rather violet than blue.

The percentages of starch in dried specimens of bread, potato, and fine white wheat flour (taking 1 gram to the liter) were estimated with the following results :

	Per cent.
Bread	41.72
Potato	38.64
Flour	45.60

Of substances containing little starch peanuts and chocolate beans were taken, one trial being made after the fat had been removed by repeated washing with ether, the other before its removal. In both cases the solutions gave no perceptible color with iodine.

In Thorpe's Dictionary of Applied Chemistry, Vol. 3, p. 565, it is stated that when iodide of starch does not contain an excess of iodine, alcohol, ether, carbon bisulphide, or benzene fails to extract any iodine from it. To verify this I took 20 mgs. of starch, added less than one-fifth the iodine necessary to produce the maximum color, diluted to 250 cc., and added chloroform. After shaking vigorously for a few minutes the blue color disappeared from the solution and the chloroform globules were decidedly violet. This seems to show that the iodide, *in the wet state at least*, is acted upon by chloroform. A like result was obtained with carbon bisulphide.

As a general conclusion it appears that, on account of the dissociating effect of water on starch iodide, the method is available only with substances containing a large amount of starch, and is best used when the substances compared contain starch in proportions not widely differing. In fact, the solutions to be colorimetrically compared must be in all respects under conditions very nearly identical. This greatly narrows the limits within which this method is available in the examination of food materials, though occasionally cases may present themselves in which it will have a certain value.

The results of all the experiments made seem to confirm the belief that the so-called iodide of starch, if a chemical compound, is one very easily dissociated, by rise of temperature, by increase of the amount of solvent water, and by the introduction of another liquid, such as chloroform, etc., of superior solvent power.

Contribution from the Chemical Laboratory of Dartmouth College.

SILVER HYDRIDE.

By Edwin J. Bartlett and William F. Rice.

Hydrogen forms binary compounds with all the non-metallic elements. The most generally known hydride is water; the hydrides of sulphur and the halogens are acids; other well known ones are ammonia, NH_3, phosphine, PH_3, methane, CH_4, hydrogen peroxide, H_2O_2, arsine, AsH_3, and stibine, SbH_3.

Many cases occur in electrolysis, where the metal used as the negative electrode absorbs hydrogen. Examples of this are palladium, platinum, iron, nickel, gold, silver and aluminium, but the action here is without doubt almost entirely physical.

In a different manner, however, hydrides have been formed of two of the metals above mentioned. Palladium has been found to be able to absorb hydrogen to a most remarkable degree; namely, to almost one thousand times its own volume.

During this process of absorption it was found, first by Graham,[1] in 1866, and verified later by others,[2] that a definite compound of palladium was formed at about 100° C., having the composition indicated by the formula Pd_2H, and that this compound continued to occlude or absorb hydrogen, with or without the further addition of heat. This hydride could not be obtained by precipitation with the chloride or sulphate and hypophosphorous acid,[3] but the metallic sponge thus formed had the property similar to the cupric hydride discovered by Merrill,[4] of indefinitely decomposing the acid with the evolution of hydrogen. In 1862 Wanklyn and Carius[5] prepared a hydride of iron from ferrous iodide and zinc ethyl, but did not determine the formula.

Hydrides of potassium[6] and sodium are known. Both are made[7] by heating the metals in an atmosphere of hydrogen. Potassium hydride, K_2H, is formed at 200° C., sodium hydride, Na_2H, requires a higher temperature.

Recently lithium hydride,[8] LiH, has been prepared and analyzed. It decomposes water with the evolution of hydrogen.

Two hydrides of copper are known. Cuprous hydride, CuH or Cu_2H_2, was discovered in 1844 by Würtz.[9] The existence of this hydride has been denied by Berthelot,[10] who claimed that the so-called hydride was a mixture of water, oxygen and phosphorus, or perhaps a complex phosphated hydroxide of copper, formed by the mixture of several compounds. Würtz subsequently maintained his side and pointed out the errors in Berthelot's work.

Cupric hydride was discovered last year by Mr. W. H. Merrill in the Chemical Laboratory of this College. Würtz had obtained his hydride by precipitating copper sulphate with barium hypophosphite, and it is reasonable to suppose that at some stage in the process he must have had cupric hydride. Mr. Merrill in his work used hypophosphorous acid itself and took great care to prevent the cupric from changing to cuprous hydride and then to the metallic sponge.

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[1] Phil. Mag. (4), **32**, 516; Proc. Roy. Soc., **15**, 502; **16**, 422.

[2] Troost and Hautefeuille: Compt. Rend., **78**, 686, 968; Dewar: Phil. Mag., **47**, 334; Favre: Compt. Rend., **71**, 214; **77**, 649; **78**, 1257: **68**, 1306, 1520: Thorne: Ztschr. phys. Chem., **3**, 69; **17**, 1.

[3] Engel: Compt. Rend., **110**, 786.

[4] This JOURNAL, **17**, 185.

[5] Ann. Chem. Phys., **120**, 69.

[6] Gmelin's Handbook, (Watt's Trans.), **3**, 17.

[7] Troost and Hautefeuille: Compt. Rend., **78**, 807.

[8] Guntz, Compt. Rend., **122**, 244.

[9] Compt. Rend., **18**, 702; Ann. Chim. (3), **11**, 250.

[10] Compt. Rend., **89**, 1005.

His analyses showed the formula to be CuH_2. As before mentioned, this substance has the power of indefinitely oxidizing hypophosphorous to phosphorous acid, the action having no effect on the hydride and taking place at the ordinary temperature. He describes the hydride as a reddish-brown sponge-like mass when freshly prepared, changing to a chocolate-colored powder on being freed from acid and boiled in water.

In carrying on the work begun by Mr. Merrill last year, particular attention was given to finding and analyzing the hydride of silver. We also obtained a hydride of mercury, but have made no quantitative determinations.

The silver hydride was prepared by precipitating a dilute solution of silver nitrate with dilute hypophosphorous acid in excess. The mixture becomes first wine-colored, changing almost immediately to black, often showing a silvery lustre on the sides of the containing vessel. The rapidity of the color change is lessened as the original solutions are made more dilute. At this stage it passes through filter-paper, staining it black. After standing two or three minutes a black product begins to settle in small spongy flakes. In about five minutes the supernatant liquid is decanted off. The yield of precipitate is not very large, but longer standing soon changes the hydride to silver. The decanted liquid on standing or boiling deposits all the remaining silver in a sponge.

The precipitate is immediately washed with cold water until free from acid, thoroughly dried at about 60° C. to constant weight and ignited in a porcelain crucible to constant weight. The product is then bright metallic silver.

Considerable difficulty is found in getting good samples of the hydride, the precipitate when dry appearing lighter in color the greater the proportion of silver present. This was proved to be the case when the computations came to be made.

The formula AgH requires 99.074 per cent. of silver, the atomic weight of Ag being 107.9 and that of H 1.008.

Fourteen determinations resulted as follows :

Substance taken. Gram.	Silver obtained. Gram.	Per cent. silver.
0.2613	0.2597	99.38
0.0268	0.0266	99.23
0.06945	0.0689	99.21
0.05975	0.05925	99.16
0.08525	0.08443	99.04
0.03865	0.03841	99.38
0.14359	0.14277	99.43
0.1647	0.16322	99.10
0.09563	0.09500	99.34
0.0809	0.08041	99.39
0.16339	0.16240	99.39
0.16353	0.16213	99.14
0.20940	0.20815	99.40
0.16552	0.16465	99.47

Average, 99.289 per cent. ; difference from computed value, 0.22 per cent.

To test the accuracy of the above results several experiments were performed by treating in the same manner some of the silver sponge obtained in the course of preparing the hydride. Amounts varying from 0.18783 gram to 3.75008 grams of the sponge were taken and in all cases the silver found was between 99.835 and 99.936 per cent.

Silver hydride is not decomposed by water, nor does it evolve hydrogen in the presence of hypophosphorous acid.

DARTMOUTH COLLEGE,
JUNE, 1896.

Contribution from the Laboratories of the Massachusetts Institute of Technology.

XV.—ON THE VOLATILITY OF FERRIC CHLORIDE.

BY HENRY P. TALBOT.

The analytical examination of iron-bearing bodies involves the frequent heating of ferric chloride solutions, as well as the occasional continued heating of the residues which such solutions leave after evaporation, and the accuracy of such analyses is dependent upon the permanency of the iron under the prevailing conditions. The writer has frequently noted an apparent deposit of ferric chloride upon the outer edge of watch-glasses used as covers for solutions during evaporation, which suggested a possible loss of iron. An examination of the literature revealed the existence of conflicting statements bearing upon the volatility of ferric chloride, and an absence of data relating to its behavior under such conditions as prevail when a residue of chlorides and silicic acid is heated to accomplish the dehydration of the latter, as in the analysis of silicates.

Fresenius,[1] in 1867, published a series of experiments from the results of which the conclusion is drawn that no loss of ferric chloride occurs during the processes of evaporation, either when the solutions are rapidly boiled, or indeed, when the residues are subjected to prolonged heating at the temperature of the water-bath. The procedure adopted for the determination of the iron was that of titration with stannous chloride, and the determination of the excess of the latter by titration with iodine. No data are presented bearing upon a possible loss of the chloride at temperatures as high as 125° or 130° C., at which silicic acid is commonly dehydrated.

But, on the other side of the question stands the statement of Vogel,[2] made in 1869, that traces of ferric chloride are volatilized from aqueous solutions, even at temperatures below 100° C., and that such volatilization occurs at temperatures as low as 30° C., in the presence of ether. He calls attention to the obvious possibility of loss of iron during the course of analysis, as a result of this volatility.

More recently, Browne[3] has made a statement to the effect that a loss of ferric chloride is to be feared "if its solution be too strongly heated," which he seems to consider a possible source of error in the analysis of iron ores, against which the chemist is to be cautioned. It seemed desirable, in the light of these varying statements, that the subject should be again investigated.

The experiments which Vogel described were repeated with substantially the results which he published, with the one exception, that but little difference was observable qualitatively between a very concentrated aqueous solution of ferric chloride, and an ethereal solution. A paper (frequently moistened throughout the day with potassium sulphocyanate solution), which covered a beaker containing the ether solution, showed some evidence of iron on standing over night. To determine qualitatively whether the ether vapor would promote the volatilization of the ferric chloride to a marked degree, an ethereal solution was subjected to distillation on the water-bath, but the distillate, after shaking with water, yielded only the faintest trace of iron, and a similar result was recorded when ether vapor was passed into a concentrated boiling solution of the chloride. No quantitative determinations were attempted, since in the light of other experiments, these seemed superfluous.

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[1] Ztschr. anal. Chem., **6**, 92.

[2] N. Rep. Pharm., **18**, 157.

[3] J. Anal. Appl. Chem., 1891, 342.

The ferric chloride solutions employed in the following experiments were prepared from the sublimed chloride, and were themselves very nearly neutral. They were measured from a burette into a porcelain dish, or small casserole, and evaporated as described in the various paragraphs below. The residues were moistened with 15 cc. of hydrochloric acid (1.12 sp. gr.), and brought into solution by warming. The reduction was effected while hot, by the cautious addition of stannous chloride solution,[1] avoiding the addition of more than a few drops in excess, after which this excess of tin was oxidized by the addition of 10 cc. of a mercuric chloride solution (50 grams to the liter). After an interval of three minutes, to allow complete precipitation of the mercurous chloride, the ferrous iron was titrated with a standard solution of potassium bichromate, the end-point chosen being that at which no blue could be detected after a contact of the iron and ferricyanide solutions lasting thirty seconds. The end-point may be determined with certainty and accuracy, by placing upon a white surface, such as a glazed porcelain tile, several small drops of the indicator solution (which has been freshly prepared, and so far diluted that it retains but little color[2]), mixing a drop of the iron solution with one of these, and at the end of the thirty seconds, mixing a second drop of the solution, with the drop of the indicator next the first test. If ferrous iron is present, causing precipitation during the interval of thirty seconds, the first portion will be seen to be darker than the fresh mixture. The end-point has been reached only when no difference in shade can be detected. Carried out in this way, the bichromate process for the determination of iron may be considered to be thoroughly reliable. The number of tests required to fix the end-point are small, particularly when the character of the material under examination is approximately known; and when the great advantage which the bichromate process offers in the use of hydrochloric acid solutions is considered, the time consumed by this process compares favorably with that necessary for the more popular permanganate process.

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[1] Made by allowing hydrochloric acid to act upon metallic tin until action ceases, and diluting with an equal volume of water.

[2] The solution of a crystal of potassium ferricyanide of the size of a pin head in 25 cc. of water is ample.

The potassium bichromate solutions used were approximately, decinormal, and fiftieth normal. They were standardized against iron wire, and the iron contents of the ferric chloride solutions was determined by titration with these solutions, according to the procedure outlined above. The reagents were carefully tested for iron.

Behavior of Ferric Chloride Solutions when Heated.

The first ferric chloride solution used contained, in 25 cc., 0.2201 gram iron (Fe); the mean of four determinations, 0.2205, 0.2202, 0.2199, 0.2199.

Of this solution 25 cc. evaporated to dryness on the water-bath, yielded 0.2201, 0.2201, and 0.2205 gram Fe; mean, 0.2202 gram Fe.

Of the same solution 25 cc., acidified with 15 cc. of hydrochloric acid (1.12 sp. gr.), and evaporated on the water-bath, yielded 0.2200, 0.2200, 0.2203 gram Fe; mean, 0.2201 gram Fe.

Of the same solution 25 cc., with 15 cc. of hydrochloric acid, evaporated to dryness on the water-bath, and the residue subsequently heated for two hours (the time usually assigned as necessary for the dehydration of silicic acid) at 130° C., yielded 0.2205, 0.2203, 0.2199 gram Fe; mean, 0.2202 gram Fe.

The titrations above were made with decinormal potassium bichromate solution only. In the experiments cited below, the decinormal solution was added until the end-point was nearly reached, and the titration then completed with fiftieth normal solution in the hope that small differences in the amounts of iron present might be more readily detected. It is perhaps doubtful if the results may properly be considered to be more accurate than with the decinormal solution alone. They are presented as cumulative evidence.

A second ferric chloride solution was found to contain, in 25 cc., 0.1741 gram Fe, as a mean of six determinations.

Of this solution 25 cc. evaporated on the water-bath, and the residue subsequently heated for two hours at 130° C., yielded 0.1739, 0.1738, 0.1742, 0.1739, 0.1739, 0.1737 gram Fe; mean, 0.1739 gram Fe.

Of the same solution, 25 cc. evaporated to dryness on a hot plate, and the residue heated as above, yielded 0.1742, 0.1737, 0.1741, 0.1742 gram Fe; mean, 0.1740 gram Fe.

In order to test an extreme case, three portions, of 25 cc. each, of the ferric chloride solution were evaporated to dryness on the hot plate, and the residues subsequently heated over the free flame for three minutes in each of two instances, and for half an hour in the third. The amounts of iron found in the residues were 0.1735, 0.1738, and 0.1736. While these figures indicate a slight loss of iron, the amount is less than 0.4 per cent. of the iron present, even under these extreme conditions.

The foregoing results confirm the statements made by Fresenius, that ferric chloride is not volatilized by boiling its solutions, and show, in addition, that no loss of iron ensues on heating the residues from these solutions in the hot closet, at 130° C. Browne states, in the paper already cited, that a filter paper moistened with potassium sulphocyanate solution, and held above a boiling ferric chloride solution will give ready proof of the presence of the latter in the escaping vapors. Repeated experiments bearing upon this point showed that the evidences of the presence of iron upon the filter paper, when they were to be found at all, were of such a character as to indicate that minute drops were projected upward by the boiling liquid, rather than that a volatilization of the iron, in a strict sense, had occurred.

Other experiments were made in which several portions of a very concentrated ferric chloride solution, both with and without the addition of acid, were distilled in a flask provided with an exit tube so bent as to make mechanical transfer of iron from the flask to the condenser impossible, and the distillation cautiously continued to dryness. In no instance could any iron be detected in the distillate, until the ferric chloride had separated from solution, and had been volatilized in the moist, acid atmosphere by the overheating of the sides of the flask. The conditions within the distillation flask, as a result of the partial condensation and return of the aqueous vapor charged with hydrochloric acid, differ from those which prevail during evaporation in open dishes, and are probably more favorable to the volatilization of the iron salt at the moment of its separation from solution. As is well known, ferric chloride solutions lose acid during evaporation in open vessels, with the formation of basic salts, which may reasonably prevent the possible volatilization of the unchanged chloride, until it, in turn, has become basic.

In order to study a little more closely the behavior of the chloride during evaporation, and when heated to a definite temperature, 25 cc. of a solution (containing 0.2210 gram Fe), were placed in a small flask immersed in an oil-bath, and a slow current of dry air passed over the solution at a temperature of about 100° C., until it had evaporated to dryness, after which the temperature was raised to 195° C. for an hour or more. The air current, after leaving the flask, passed through water, to retain any ferric chloride which it might carry with it. Only a slight coloration could be obtained with potassium sulphocyanate in this water, and the residue in the flask yielded 0.2203 gram Fe. A second portion heated to 250° C. yielded 0.2204 gram Fe. Since the boiling-point of ferric chloride is stated by Friedel and Crafts[1] to be 280°-285° C., it appears that very little, if any, of the iron remains as unaltered ferric chloride, otherwise the trifling loss of iron at a temperature so near the boiling-point of the chloride could hardly be explained.

Behavior of Ferric Chloride in the Presence of Ammonium Chloride.

It seemed desirable to extend the experiments in such a way as to include solutions which, beside the ferric chloride, should also contain ammonium chloride.

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[1] Compt. rend., **107**, 301.

To three portions of 25 cc. each, of a ferric chloride solution (containing 0.1739 gram Fe), was added 1 gram of ammonium chloride, the solution evaporated to dryness on the plate, and the residue heated for two hours at 130° C. The amounts of iron found in the residues were 0.1742, 0.1742, 0.1739 gram Fe (mean, 0.1741 gram Fe), indicating that the presence of the ammonium salt does not occasion a loss of iron within the limits named.

As would be expected, stronger heating in the presence of the ammonium salt led to volatilization of the iron. A portion of the solution, prepared as above, when evaporated to dryness on a hot plate and allowed to remain on the plate until the ammonium chloride had been slowly, but completely expelled, still yielded 0.1718 gram Fe, while two other portions (each containing 0.1747 gram Fe), which were heated over a free flame until ammonium chloride fumes first appeared, yielded 0.1745 and 0.1746 gram Fe. Still other portions of the same solution which were strongly heated over a free flame until the ammonium salt was entirely expelled, yielded only 0.1542 and 0.1643 gram Fe.

Behavior of Ferric Chloride in the Presence of Nascent Chlorine.

To determine the behavior of ferric chloride in the presence of nascent chlorine, 25 cc. of a solution (containing 0.1739 gram Fe), were mixed with 5 cc. of a mixture of three parts of hydrochloric acid (sp. gr. 1.2) and two parts of nitric acid (sp. gr. 1.42), and the mixture was evaporated to dryness on the plate, after which the residues were heated for two hours at 130° C. The iron found in each of three such portions amounted to 0.1730, 0.1730, 0.1729 gram. A second series of three portions (each containing 0.1747 gram Fe), was evaporated on the water-bath, and heated as above. These yielded 0.1742, 0.1737, 0.1738 gram Fe. The data furnished by these experiments indicate a tendency toward a loss of iron in the presence of the nascent chlorine, or the nitric acid. The maximum deficiency represents only 0.6 per cent. of the total iron.

In summarizing, it may be said that the results show that no loss of iron, in the form of ferric chloride, is to be feared under the conditions which prevail in ordinary analytical procedures, unless residues containing also ammonium chloride are overheated, or, in the presence of aqua regia, where a small, but appreciable loss of iron appears to be possible.

In conclusion, acknowledgment is gladly made of the writer's indebtedness to Messrs. R. F. Hosford and G. M. Goodspeed for painstaking analytical work, the results of which are embodied in the foregoing discussion.

CONCERNING PROPERTIES BELONGING TO THE ALCOHOL-SOLUBLE PROTEID OF WHEAT AND OF CERTAIN OTHER CEREAL GRAINS.

By G. L. Teller.

In attempting to work out a method for the ready quantitative separation of the proteids in wheat[1] based upon the properties of those bodies as described by Osborne and Voorhees,[2] and especially in attempting to separate the gluten and the non-gluten nitrogen compounds by thoroughly extracting a small quantity of the meal with dilute salt solutions, it was found that certain discrepancies occurred which made it apparent that considerable quantities of the same nitrogen compound or compounds were soluble both in dilute salt solutions and in 75 per cent. alcohol. It had also been ascertained by an extensive series of investigations that a considerably larger quantity of nitrogen compounds was extracted by a 1 per cent. than by a 10 per cent. solution of common salt (NaCl), and that for salt solutions between these strengths there was a gradual decrease of the amount of nitrogen compounds extracted as the salt solution contained more salt. Furthermore, the decrease did not stop with 10 per cent. salt solution, but was still seen when 15 per cent. and 20 per cent. solutions were used. Thus a sample of low grade flour gave the following results: One per cent. salt solution extract contained 0.66 per cent. of nitrogen; 10 per cent. salt solution extract contained 0.48 per cent. of nitrogen; and 20 per cent. salt solution extract contained 0.20 per cent. of nitrogen to each gram of material extracted.

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[1] Full details of this work are given in Part II. of Bulletin No. 42 of the Arkansas Agricultural Experiment Station, which publication is now in press.

[2] This JOURNAL, **15**, 392-471.

With the hope of finding the cause of this feature of the question a considerable quantity of perfectly clear 1 per cent. salt extract of wheat meal was obtained. To this a sufficient quantity of dry salt was added to make a 10 per cent. solution. A considerable precipitate was produced and this was found to be largely soluble in 75 per cent. alcohol, in a clear solution of which proteids were readily detected.

If the proteids, or a portion of them, which are soluble in salt solution are insoluble in alcohol they should be precipitated by the addition of alcohol to the salt solution. When 50 cc. of the clear, filtered, 1 per cent. salt extract of wheat were mixed with sufficient strong alcohol to make the resulting mixture contain about 75 per cent., a considerable white, flocculent precipitate was produced. This soon settled, leaving a clear liquid. The liquid filtered rapidly, giving a perfectly clear filtrate. The rapidity of flocculation of the precipitate increased somewhat on heating. The concentrated filtrate gave a strong biuret reaction. In like manner a marked biuret reaction for proteids was obtained by concentrating 100 cc. of alcohol filtrate when the added alcohol was such as to make 90 per cent. of alcohol in the mixture.

In following out this line of investigation a solution was made by mixing 100 grams of wheat meal with 500 cc. of 1 per cent. salt solution, shaking at intervals for one hour and filtering at the end of three hours. The proteids insoluble in 75 per cent. alcohol were precipitated from 40 cc. of this perfectly clear filtrate by the addition of such alcohol as was necessary to make a mixture of the desired strength. An aliquot portion of the resulting clear alcoholic filtrate, corresponding to 20 cc. of the original salt solution, was evaporated to dryness in a Kjeldahl flask, and a determination made of the amount of nitrogen it contained. Similar nitrogen determinations were made when a 10 per cent., and later a 15 per cent. salt solution was used for extracting like quantities of the same wheat. In this manner is found the number of milligrams of nitrogen in the nitrogen compounds soluble in alcohol from 20 cc. of the salt solutions of the various strengths. Determinations of the total nitrogen contents of each of these salt solutions were also made and computed to milligrams in each 20 cc. of solution. The results of both of these series of determinations are shown below :

	Total nitrogen. Milligrams.	Alcohol-soluble nitrogen. Milligrams
1 per cent. salt solution	19.48	9.7
10 " " " "	18.6	8.8
15 " " " "	16.2	7.6

It was found later that a part of this alcohol-soluble nitrogen is from amides, but the amount of amides in the wheat was by no means sufficient to account for the whole of the nitrogen thus obtained, and furthermore, abundant indications of proteids were found in each case by suitably concentrating the alcoholic filtrate and applying the biuret test.

A further comparison of the extracts obtained by 1 per cent. and by 10 per cent. salt solutions was made as follows : Salt extracts were made in 200 cc. measuring flasks, as hereafter described, using 4 grams of material, so that 50 cc. of the extract would correspond to 1 gram of the sample. This quantity of extract was mixed with 250 cc. of strong alcohol and allowed to stand over night. Nitrogen was then determined in both the filtrates and the precipitates with the following results :

Precipitated by alcohol.	Nitrogen. Per cent.
1 per cent. salt solution	0.21
10 " " " "	0.23
Soluble in alcohol.	
1 per cent. salt solution	0.42
10 " " " "	0.27

A similar trial on a sample of "ship stuff" gave results as follows :

Precipitated by alcohol.	Nitrogen. Per cent.
1 per cent. salt solution	0.31
10 " " " "	0.31

It seems clear that the difference in amounts of nitrogen compounds removed from wheat by 1 per cent. and by 10 per cent. salt solutions is due to such as are soluble in 75 per cent. alcohol. Filtering hot did not materially affect the results.

A strong alcoholic solution of wheat proteids was made by mixing the meal with cold 75 per cent. alcohol. On pouring this clear extract into 1 per cent. salt solution a precipitate was produced which, when filtered off, gave a perfectly clear filtrate. Proteids in considerable quantity were detected in this filtrate by various reactions. Furthermore, the liquid was found to give the reactions characteristic of proteoses: Not coagulated by heat; a precipitate with nitric acid which disappeared on warming and reappeared on cooling; a like reaction with potassium ferrocyanide and acetic acid; precipitation by 20 per cent. sodium chloride and acetic acid. Authorities[1] also state that proteoses are precipitated by alcohol. Either we have here a proteose which is soluble in alcohol, or it is the result of the decomposition of a proteid which is soluble in alcohol, brought about by mixing the liquid with the 1 per cent. salt solution. If it be the latter, what is the explanation of the alcohol-soluble portion of the salt extract? When the alcohol solution of this salt-soluble proteid is concentrated it exhibits the properties of proteoses mentioned. It also, when concentrated somewhat, exhibits the character of gliadin solutions in alcohol, in that it is precipitated either by the addition of water or of strong alcohol.

A sample of fresh gluten was treated with hot 75 per cent. alcohol and 10 cc. of a resulting concentrated extract were poured into 90 cc. of 1 per cent. salt solution. A precipitate formed which, on the following morning, was filtered off and, by sprinkling a little pure, fine animal charcoal on the wet filter, a perfectly clear filtrate was obtained. This filtrate contained a proteid exhibiting the same proteose reactions mentioned above.

Some months previous a sample of gliadin had been prepared, at least nearly pure, by precipitating the concentrated 75 per cent. alcohol solution with absolute alcohol, and washing well with alcohol and ether, after which it was dried in a vacuum over sulphuric acid. A 75 per cent. alcohol solution of this was prepared, which, when poured into a considerable quantity of 1 per cent. salt solution, gave the usual precipitate. A clear filtrate, obtained without the use of animal charcoal, exhibited the proteose reactions.

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[1] Chittenden: Digestive Proteolysis, p. 62; Hammarsten: Physiological Chemistry, p. 26.

In the course of the work concerning the separation of proteids mentioned above a separation was made of the nitrogen compounds contained in a 1 per cent. salt solution extract of wheat meal, etc., by the method outlined below. Five grams of the material were put into a 250 cc. measuring flask; about 15 cc. of a 1 per cent. solution of common salt were added and the two mixed thoroughly by shaking. The flask was then filled nearly to the neck with the same solution, and in this condition the contents of the flask were shaken at intervals of ten minutes for one hour. At the end of this time the flask was filled to the mark with the fresh salt solution, and the whole thoroughly mixed by shaking. After settling for two hours the liquid was decanted onto a 12.5 cm. dry filter of good quality, leaving the greater part of the solid material in the flask. The liquid was always clouded but, when refiltered through the same filter, generally became perfectly clear. 50 cc. of the clear liquid thus obtained were put into a Kjeldahl digestion flask, 20 cc. of strong sulphuric acid added, and the water removed by boiling, breakage being prevented by protecting the flask by a thin sheet of asbestos cloth. When all water was driven off and the acid ceased foaming, the usual amount of potassium sulphate was added and the nitrogen determination completed. This gives the total nitrogen in the salt extract. 50 other cc. of the clear salt extract were mixed with 250 cc. of strong (94 per cent.) alcohol in a 500 cc. Kjeldahl flask. The resulting precipitate was allowed to settle over night when the liquid readily filtered off. The filter, with such precipitate as it contained, was returned to the flask, and the nitrogen determined, correction being made for a little nitrogen always found in the filter. This precipitate contains the edestin and the leucosin, as was found by suitable reactions. It does not, however, contain the amides, as these are found to be soluble in the amount of alcohol of the strength used in much larger quantities than they ever occur in the amount of wheat taken.

To separate these from the proteids in salt solution, all proteids were precipitated from 50 or 100 cc. of the clear salt extract by adding an excess of a 10 per cent. solution of phosphotungstic acid. By allowing to settle over night, a perfectly clear filtrate was obtained, of which the contained nitrogen was determined in the manner described for total salt extract nitrogen.

If the sum of the edestin, leucosin, and amide nitrogen be subtracted from the total nitrogen of the salt extract, the difference will give the nitrogen which should be credited to the alcohol-soluble proteid which has been dissolved in the 1 per cent. salt solution.

The following table gives the results of such analysis applied to twenty different samples of wheat and mill products.

Table Showing Nitrogen of Compounds Soluble in 1 Per Cent. Sodium Chloride Solution.[1]

Kind of Material.	Total nitrogen in solution.	Edestin and leucosin nitrogen.	Amide nitrogen.	Gliadin nitrogen.
Arkansas Mill Products.				
Patent flour	0.41	0.11	0.03	0.27
Straight flour	0.43	0.13	0.03	0.27
Low grade flour	0.54	0.21	0.05	0.28
"Ship stuff"	0.71	0.31	0.10	0.30
Bran	1.00	0.48	0.23	0.29
Sifted dust (outer bran)	0.50	0.16	0.20	0.14
Porter's Flours.				
Souvenir (extra patent)	0.46	0.11	0.05	0.30
0000 Boss flour (patent)	0.46	0.11	0.05	0.30
Standard flour (straight)	0.50	0.15	0.06	0.29
Strong baker's flour	0.68	0.30	0.09	0.29
Red dog (low grade)	0.97	0.45	0.25	0.27
Winter Wheats.				
Red, Arkansas	0.72	0.31	0.12	0.29
Red, Arkansas (harvest '94)	0.52	0.19	0.10	0.23
Currell, Kansas	0.71	0.30	0.14	0.27
Zimmerman, Kansas	0.68	0.26	0.12	0.30
White wheat, Canada	0.50	0.22	0.07	0.21
Oregon white	0.49	0.20	0.07	0.22
Spring Wheats.				
Red wheat, South Dakota	0.81	0.35	0.17	0.29
Red Fife, North Dakota	0.60	0.25	0.09	0.26
Red Fife, Minnesota	0.64	0.28	0.11	0.25

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[1] Figures show nitrogen in each compound in per cent. of 1 gram of substance examined.

An examination of this table will show that the nitrogen from the alcohol-soluble proteid which is entered in the table under the head of gliadin nitrogen, is for 16 of the samples practically a constant. The average for these 16 samples is 0.28 per cent. of nitrogen for 1 gram of material. Many results, which it is thought unnecessary to give, show that the same would have been true if a 10 per cent. salt solution had been used, except that the quantity thus extracted would have been less. There is a great variation in the amounts of the other nitrogen compounds contained in these various samples. The only reasonable explanation of these facts seems to be that an alcohol-soluble proteid which is somewhat soluble in 1 per cent. salt solution and less so in 10 per cent. salt solution exists in considerable quantities in the wheat.

It seems evident that this proteid is gliadin and it appears from the behavior described that gliadin is not changed when it is dissolved in salt solution, but that it remains gliadin. With the exception of being readily soluble in 75 per cent. alcohol, and but slightly soluble in dilute salt solutions, it possesses what have been set aside as the characteristic reactions of proteoses. Apparently it was this body which was found by Osborne and Voorhees in their salt solution extracts and was designated by them as a proteose and a proteose-like body under captions V. and VI.

Four results for alcohol-soluble proteid in the table above vary to a considerable extent from the average of the other sixteen. Of these, one is the sifted contents of the "dust room" of the mill where a portion of the samples were obtained. It consists of the outermost portion of the bran, and contained none of the interior of the grain. The alcohol-soluble nitrogen here obtained is 0.14 per cent. In all these samples the nitrogen soluble in 75 per cent. alcohol had been determined by a method which it is believed gives quite accurate results. In this sample the total amount of nitrogen soluble in hot 75 per cent. alcohol was 0.36 per cent. Of this, 0.20 per cent. should be credited to amides. The difference, or 0.16 per cent., represents that from the total gliadin in the material, and shows why a greater amount was not in solution in the 1 per cent. salt extract. That this alcohol-soluble proteid of the outermost bran is really gliadin was shown by diluting the suitably concentrated extract with water and with absolute alcohol. In each case a precipitate was produced. Two other samples of the series, which show an unusually low amount of alcohol-soluble proteid in solution were white wheats, each of which was found to contain a very low proportion of gliadin in comparison with the other samples. The remaining irregular sample is an Arkansas red wheat of the harvest of 1894. These include all samples which have been examined in this way.

In the alcohol solution (75 per cent.) gliadin has not been found to exhibit the reactions of proteoses with common salt. The addition of large quantities of salt in bulk, either with or without acetic acid, was not found to cloud it in the least. When salt in solution is added a precipitate will be produced, but in such cases this seems to be attributable, in part at least, to the dilution of the alcohol with water. It has been pointed out by the authors named above, that gliadin is soluble in considerable quantities in pure water but is precipitated from such solutions by the addition of a very small quantity of salt. The experiments here recorded show that the precipitation is not complete.

The solubility of gliadin in salt solutions accounts for the fact that when flour is treated directly with large quantities of such liquid no gluten is formed. It also has an important bearing upon the determination of gluten in wheat or flour by the usual mechanical method of washing away the starch and weighing the residue.

Twelve grams of Porter's "Standard" flour from spring wheat, was made into a dough with 10 cc. of 1 per cent. salt solution, and allowed to stand for one hour. It was then tied in a linen cloth and worked between the fingers in one liter of the same salt solution for one hour. It having been found impossible to obtain a clear filtrate from the solution direct, it was heated nearly to the boiling-point. One hundred and seventy-five cc. of a nearly clear filtrate from this were evaporated to about 30 cc., and enough strong alcohol added to make the mixture contain 75 per cent. Ten cc. of a perfectly clear filtrate from this showed much cloudiness on adding a few drops of phosphotungstic acid, which cloudiness disappeared on standing, a precipitate being formed. The remainder of the alcohol solution when concentrated gave, in repeated trials, distinct biuret reaction for proteids,[1] the same rose color being exhibited as when gliadin is treated.

It has beed found by a large number of trials, that the so-called true gluten obtained by mechanical washing away of the starch, and computing the remaining proteids from the nitrogen contents of the crude gluten obtained, gives results which are much too low when compared with the sum of the gliadin and glutenin in the sample examined. The explanation is here apparent. An indefinite amount of gliadin is dissolved and washed away. In view of this fact the mechanical method of determining the gluten in wheat and flour is even more unsatisfactory than it has been thought to be.

Having found the above described properties of the alcohol-soluble proteid of wheat, an effort was made to determine whether or not the proteose bodies found by Dr. Osborne[2] in the water or salt solution extracts of oats, rye and barley, and by Drs. Chittenden and Osborne[3] in similar extracts from maize, may be attributable to the alcohol-soluble proteids of those grains. To that end extracts of each were made with 75 per cent. alcohol and with 1 per cent. salt solution.

Of each clear filtered salt solution extract, 25 cc. were mixed with 125 cc. of 94 per cent. alcohol. The resulting precipitates were filtered off, and the clear filtrates were each found to possess the following reactions in common with a solution prepared from wheat in like manner: A precipitate upon dilution either with water or with absolute alcohol; a precipitate or cloud with phosphotungstic acid, which precipitate dissolves on warming and reappears on cooling;

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[1] The delicacy of the biuret reaction for this proteid may be increased by using a very small quantity [2 cc.] of the concentrated solution, an equal amount of the strongest caustic potash solution, and, after adding the few drops of copper sulphate, adding also about one cubic centimeter of strong alcohol. After shaking the mixture gently the color will be concentrated in the clear alcohol which rises to the top.

[2] Conn. Exp. Sta. Reports, 1890 and 1894.

[3] This JOURNAL, **13** and **14**.

nitric acid does not produce a precipitate in such dilute alcohol solutions.

Of each alcohol extract, 25 cc. were mixed with 125 cc. of 1 per cent. salt solution. A clear filtrate from the resulting mixture gave in each case reactions for proteids. The resulting precipitates dissolved more or less completely on warming, and reappeared on cooling. With nitric acid this solution from wheat gave a slight cloud, which disappeared on warming. With rye solution no change was produced until cooled with ice. A dense cloud then appeared, while a similar tube of liquid without the acid remained perfectly clear. This cloud disappeared on adding strong alcohol as well as on warming. In the solution from barley with nitric acid a similar, but less marked cloud appeared on cooling with ice. No precipitate with nitric acid was obtained in these dilute solutions from either corn or oats. However, certain other reagents gave, in each case, precipitates which dissolved on warming and reappeared on cooling. A nearly clear water solution obtained by mixing a 75 per cent. alcohol extract of corn with a large quantity of water gave a precipitate with nitric acid which did not dissolve, but increased on warming. When, however, a quantity of strong alcohol was added to the liquid, the precipitate immediately dissolved, and remained in solution even when cooled with ice.

With each grain, including wheat, the clear alcohol extract of the meal gave precipitates in the cold with phosphotungstic acid and with tannic acid, each being in solution in 75 per cent. alcohol. In each instance the precipitate dissolved on warming, and reappeared on cooling. With nitric acid the liquid became more or less yellow on boiling, but, as has been shown above, the compound of this acid with these proteids is readily soluble in dilute alcohol. With phosphotungstic acid the cloud, which at first dissolved, reappeared when the liquid was kept near its boiling-point for a short time. In the alcohol extract of corn the precipitate with tannic acid is slight, even with much of the reagent. It may be readily seen if the strong solution of the proteid be diluted with an equal bulk of 75 per cent. alcohol, sufficient reagent added, and the whole cooled with ice. With mercuric chloride in solution in 75 per cent. alcohol, an abundant precipitate was given in the alcohol extracts of wheat and of oats, which precipitate dissolved on warming, and reappeared on cooling. The alcohol extracts of corn, rye, and barley did not give precipitates with this reagent. It appears, therefore, that these proteids are alike and yet different.

The foregoing facts support the belief that the proteose bodies which have been found in the water or dilute salt extracts of these various grains, except corn, are really the alcohol-soluble proteids, small quantities of which have been carried into solution, and there exhibit their characteristics unchanged. Furthermore, these alcohol-soluble proteids are seen to possess certain properties which have been thought to be characteristic of proteoses.[1]

CHEMICAL LABORATORY OF THE ARKANSAS
AGRICULTURAL EXPERIMENT STATION,
FAYETTEVILLE, ARKANSAS.

SILICIDE OF CHROMIUM.

BY G. DE CHALMOT.

Moissan[2] obtained a silicide of chromium of the formula $SiCr_2$, hy heating silicon with an excess of chromium. When chromium sesquioxide, charcoal and silica (the latter in excess) are heated in an electric arc furnace, a different compound of the formula Si_2Cr, can be obtained. This compound crystallizes in long needles which are gray, and have a strong metallic luster. The crystallizing power of this compound is very pronounced, for the needles were found in a chromium-silicon alloy with only 42.65 per cent. of silicon, and they were very well developed in an alloy with 59.11 per cent. of silicon.

Cold hydrochloric acid and aqua regia have no perceptible effect on this compound, but hydrofluoric acid attacks and dissolves it. This reaction I made use of for determining the composition of the compound. I was unable to obtain a sufficient quantity of pure crystals for analysis. I therefore determined the composition of material to which some silicon adhered, and deducted from the total amount of silicon that part which was insoluble in hydrofluoric acid, and was not chemically combined. I thus found the amount of silicon which was united with chromium. For analysis the material was sifted through linen, and fused with sodium carbonate and potassium nitrate.

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[1] Charles: Physiological Chemistry, 1884, p. 117; Hammarsten, Mandel: Physiological Chemistry, 1893, p. 25; Chittenden: Digestive Proteolysis, 1894, p. 62; Watts' Dictionary of Chemistry, 1894, **4**, 331.

[2] Compt. Rend., **121**, 624.

	I.	II.
Total silicon	59.11	53.40
Free "	13.84	4.71
Combined silicon	45.27	48.69
Chromium	41.36	45.90

The composition of the crystals therefore is:

	Found.		Calculated for
	I.	II.	Si_2Cr.
Si	52.26	51.48	52.12
Cr	47.74	48.52	47.88

The specific gravity of II. was found to be 4.393.

WILLSON ALUMINUM CO.,
SPRAY, N. C.

Contribution from the Chemical Laboratory of Wesleyan University.

PARAISOBUTYLPHENOXYACETIC ACID.

BY W. P. BRADLEY AND F. KNIFFEN.

Phenoxyacetic acid has been made by Giacosa,[1] by Heintz[2] and by Fritsche.[3] The homologous paraisobutylphenoxyacetic acid was made according to the methods both of Giacosa and of Fritsche. The former method was much simpler in execution, but the latter, as giving much the better yield, is described:

Ten grams paraisobutylphenol were added to 3 grams sodium hydroxide, dissolved in a little cold water; 19 grams chloracetic acid were added to 8 grams sodium hydroxide, similarly dissolved; and the two salts so obtained were brought in pasty condition into an iron pan and heated gently for one hour and a half with constant stirring. The mass became brown, but exhibited none of the deep red color noticed by Fritsche when using the simple phenol. When cool the product was thoroughly neutralized with sulphuric acid, and the watery layer containing sodium sulphate removed. To separate the new compound from the unchanged phenol, advantage was taken of its greater acid strength. The mixture of the two was made distinctly alkaline with sodium carbonate solution and the unchanged phenol was removed with the aid of ether. The resulting straw-colored liquid was evaporated to small bulk, acidified, and extracted with ether. The residue left after evaporating the ether was crystallized twice out of ligroïn, and showed then a constant melting-point of 86°.5. The yield was 9.1 grams, or 66.5 per cent. of the theoretical.

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[1] J. prakt. Chem., [2], **19**, 396.

[2] Jrsb. Chem., 1859, 361.

[3] J. prakt. Chem., [2], **20**, 269.

Analysis.

	Calculated for $C_{10}H_{13}OC_2H_3O_2$.	Found. I.	II.	III.
C	69.23	68.92	...	69.08
H	7.69	7.95	7.89	8.03

The new acid is a cream-white solid, practicably insoluble in water. It dissolves very easily in the usual organic solvents, of which many were tried in search of a good purifying medium. Hot ligroïn is the only solvent, however, which deposits clean cut crystals, and this was invariably used. The crystals are radial in structure. They possess a faint, not unpleasant, and characteristic odor, difficult to describe.

Except with mercury and iron, the acid gives salts more or less soluble in water. Those of the alkalies as well as of zinc and magnesium are quite soluble. Solutions of the ammonium salt decompose on boiling with gradual volatilization of the acid, which is betrayed by its odor. The barium and zinc salts were prepared and analyzed.

Barium Salt, $(C_4H_9C_6H_4OCH_2COO)_2Ba,\frac{1}{2}[2\frac{1}{2}]Aq$.—This salt is best obtained by the action of the free acid on barium carbonate suspended in hot water. The resulting solution on evaporation to small bulk, yields the salt ordinarily in the form of small snow-white crystals having a large nucleus surrounded by short, hair-like processes, and resembling somewhat a chestnut burr in appearance. These are permanent over sulphuric acid, but lose half a molecule of water when heated to constant weight at 110°.

Analysis.

	Calculated for $(C_{10}H_{13}OC_2H_2O_2)_2Ba.\frac{1}{2}Aq$.	Found.
H_2O	1.61	1.94
Ba	24.46	24.66

On one occasion a dilute solution of the barium salt deposited crystals having a small nucleus surrounded by relatively large, transparent, radiating arms. These were found, on analysis, to contain two and one-half molecules of water of crystallization. All attempts to secure a further crop of these more highly hydrated crystals failed.

The ordinary variety of the salt dissolves in water at 15° to the extent of 46 parts in 10,000.

Magnesium Salt, $(C_4H_9C_6H_4OCH_2COO)_2Mg,5\frac{1}{2}Aq$.—This salt was prepared by carefully precipitating the barium salt with magnesium sulphate. On evaporation, the filtrate deposited crystals in which fan-like projections radiate from a rather prominent center. The air-dried salt lost its water of crystallization after eight days' drying over sulphuric acid.

Analysis.

	Calculated for $(C_{10}H_{13}OC_2H_2O_2)_2Mg,5\frac{1}{2}Aq$.	Found.
H_2O	18.44	18.47
Mg	4.47	4.40

A magnesium determination was made in the anhydrous salt :

	Calculated.	Found.
Mg	5.48	5.44

The anhydrous salt is hygroscopic. The crystallized salt dissolves in water at 20° to the extent of 13 parts in 10,000.

Esterification of the Acid.—The esterification of the acid proceeds spontaneously to a considerable extent when its alcoholic solutions are allowed to stand even at the ordinary temperature, as may be perceived by the odor when such solutions are allowed to evaporate. The methyl ether, obtained in the usual way by the action of hydrochloric acid gas on the methyl alcoholic solution of the acid, is a wine-colored, viscous liquid of faint, spicy odor. It stiffened in a freezing mixture of ice and salt, but deposited no crystals, even when exposed for some time. Lack of material prevented its purification by distillation, and it was accordingly not analyzed, but was utilized for the preparation of the acid amide.

The Acid Amide, $C_4H_9C_6H_4CH_2CONH_2$.—A portion of the methyl ether was exposed in a test-tube for five days to the action of twice its volume of concentrated ammonia. The solid cake which had then formed was broken up in a mortar, thoroughly washed with cold water, and crystallized out of very dilute alcohol. The solution becomes milky on cooling, but later deposits the amide in thin, flat, snow-white plates, which when pure, are inodorous and melt at 134°.

Analysis.

	Calculated for $C_{10}H_{13}OC_2H_2ONH_2$.	Found.
N	6.76	6.91

The amide is practically insoluble in cold, difficultly in hot water. In ordinary organic solvents, except ligroïn, it is quite soluble, but separates in poorly defined crystalline masses. From solution in hot ligroïn it separates in massive, well-shaped crystals.

The Anilide, $C_4H_9C_6H_4OCH_2CONHC_6H_5$.—One gram of aniline and two grams of acid were heated for one hour in a short test-tube at 150°. The resulting clear red liquid was poured, while still hot, into cold water. It gradually became viscous, and when stirred with a glass rod became solid. The yellowish-brown mass was washed consecutively with dilute sodium hydroxide, hydrochloric acid, and water, and then dissolved in dilute alcohol. The crystals obtained in this way were somewhat discolored and melted at 97°. They became pure white after a single crystallization out of ligroïn,[1] but the melting-point remained unchanged.

Analysis.

	Calculated for $C_{10}H_{13}OC_2H_2ONHC_6H_5$.	Found.
C	76.33	76.13
H	7.42	7.37
N	4.95	5.13

The anilide is insoluble in water, soluble in organic solvents. Alcoholic solutions yield long individual needles; acetone, clusters of needles; benzene, chloroform, and carbon disulphide, radiating crystalline masses; glacial acetic acid, beautiful fern-like crystals. It appears not to crystallize at all from ether, but is deposited in oily condition.

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[1] It is well known how persistently many anilides retain a slight degree of discoloration. The very striking manner in which the anilide just described was decolorized by the use of ligroïn, suggested the use of the same solvent for other anilides, and it was found in fact that acetanilide can be obtained in snow white needles after a single crystallization from ligroïn, in which, however, it is not very soluble.

The Metanitranilide, $C_4H_9C_6H_4OCH_2CONHC_6H_4NO_2$. — This compound was obtained from metanitraniline in the same manner as the preceding. It stiffened, but did not solidify when poured into cold water. It was crystallized twice from alcohol and was obtained in the form of yellowish-brown clusters, which were sufficiently pure for analysis.

Analysis.

	Calculated for $C_{10}H_{13}OC_2H_2ONHC_6H_4NO_2$.	Found.
C	65.85	65.72
H	6.10	6.09
N	8.54	8.72

The compound is so slightly soluble in ligroïn that this solvent cannot be advantageously employed as a purifying medium except for very small quantities. It yields, however, beautiful cream-yellow needles whose melting-point lies between 136°–139°. The compound appears not to melt sharply.

Action of Nitric Acid on the Anilide.—The attempt was made to prepare the ortho and para nitro derivatives of the anilide by direct nitration. The finely divided anilide was introduced gradually into fuming nitric acid cooled in snow, as long as it dissolved freely, and the liquid, after standing fifteen minutes, was thrown upon clean snow. The solid product was washed thoroughly with water, and then dissolved in 95 per cent. alcohol. From this solution several successive crops of crystals were obtained, but contrary to expectation, all of them possessed practically the same melting-point, indicating the formation of a single product only; and this product on analysis was found to contain, not one nitro group, as was expected, but four.

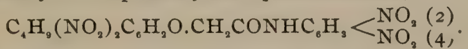
Analysis.

	Calculated for $C_{18}H_{17}N_5O_{10}$.	Found.
N	15.12	15.00

This tetranitro compound is obtained from alcoholic solutions in the form of dull yellow, warty crystals, which melt gradually between 135° and 140°. We were unable to obtain a sharp melting-point. Chloroform, benzene, and acetone deposit the substance as an oil. Most other solvents yield indistinctly crystalline masses. It is not very soluble in ether or alcohol.

Proof was next obtained that the four nitro groups are divided equally between the two benzene rings present in the compound. Four parts of the compound dissolved in alcohol and one part of potassium hydroxide, also dissolved in alcohol, were brought together and boiled three-quarters of an hour. After evaporating the greater part of the alcohol, water was added. The nitraniline thus precipitated was removed by aid of ether, and was crystallized, after evaporation of the latter, twice from alcohol. Small, bright, lemon-yellow crystals were obtained, melting sharply at 176°.5, which give the red coloration when boiled with dilute potassium hydroxide, which is characteristic for *o-p*-dinitraniline.

It should have been an equally easy task to locate the other two nitro groups in the benzene ring belonging to the paraisobutylphenoxyacetic acid, but this result was prevented by unexpected difficulties in the purification of the dinitro acid. The compound exhibited a stubborn tendency to separate from its solutions as a gummy mass, containing, to be sure, in most cases, small crystals, but these crystals in turn show the same tendency on recrystallization, so that no direct proof of their composition could be obtained. There seems no doubt, however, as already indicated, that the product obtained by the direct action of cold nitric acid on the anilide is paraisobutyldinitrophenoxyacet-*o-p*-dinitranilide,



$$C_4H_9(NO_2)_2C_6H_2O.CH_2CONHC_6H_3<\begin{matrix}NO_2\ (2)\\ NO_2\ (4)\end{matrix}.$$

The Toluides, $C_4H_9C_6H_4OCH_2CONHC_6H_4CH_3$.—The ortho and para toluides of the acid were also prepared. The melt containing the ortho derivative gave, when poured into water, a blue-black, solid mass, which crystallized out of ligroïn in long, flat, white blades, which melt at 91°. It dissolves readily in organic solvents, and is deposited from most of them, even after complete evaporation of the solvent, in well-formed crystals, usually of dendritic structure. Dilute alcoholic solutions yield only oil drops.

The paratoluide is dull gray before purification, and snow-white after. The crystals obtained by the use of ligroïn as a solvent resemble strongly those of the ortho compound, but melt at 122°. From other solvents indistinct crystalline masses are usually obtained, except from alcohol, which yields, as with the ortho compounds, oil drops.

Analysis.

	Calculated for $C_{10}H_{13}OC_2H_2ONHC_6H_4CH_3$.	Found. Ortho.	Found. Para.
C	76.77	76.54	76.59
H	7.74	7.63	7.36
N	4.71	5.05	5.07

Paraisobutylphenoxyacetphenylhydrazide, $C_4H_9C_6H_4OCH_2$-$CONHNHC_6H_5$, was obtained by heating the methyl ether of the acid with its own weight of phenylhydrazine four hours at 110°. The reaction proceeds rapidly at first with ebullition. The resulting product solidified on cooling to a mass resembling candied honey. When crystallized from alcohol or glacial acetic acid, it yielded colorless crystals melting sharply at 171°.5.

Analysis.

	Calculated for $C_{10}H_{13}OC_2H_2ON_2H_2C_6H_5$.	Found.
N	9.40	9.59

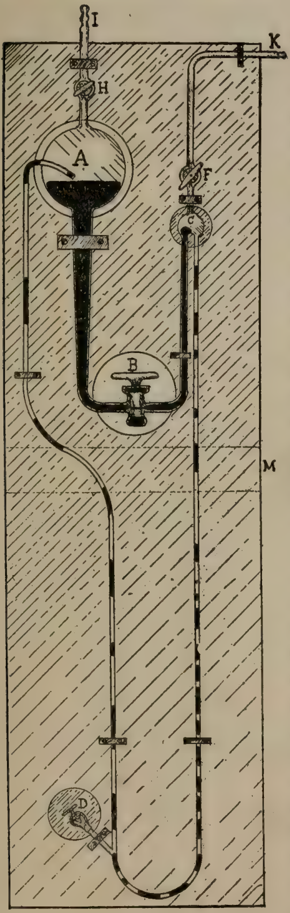
The hydrazide is easily soluble in the ordinary solvents, except ligroïn, in which it dissolves but sparingly.

Contribution from the Sheffield Laboratory of Yale University.

XLVII.—ON A SIMPLE AUTOMATIC SPRENGEL PUMP.

By B. B. Boltwood.

The following description of a simple modification of the Sprengel pump, the advantages of which are compactness, convenience, and speed in obtaining vacua of high exhaustion, may be of interest to both chemists and physicists.



The apparatus, which is fastened to a board 60 cm. in length and 18 cm. in width, consists of the bulb *A*, 6 cm. in diameter, connected by means of the tube *ABC*, in which is situated the stop-cock *B* with mercury seal, with the small bulb *C*, about 2 cm. in diameter, into which the tube *KC*, connected with the vessel to be exhausted, opens, and from which extends the fall-tube *CD*, 50 cm. in length. The continuation of *CD* is the return tube *DA*, which extends into the interior of *A* for about 3 cm. The bulb *A* is about one-third full of *clean*, *dry* mercury.

The operation of pumping is as follows: The tube *I* is connected by means of suitable thick-walled rubber tubing with a water-jet pump, which will give a vacuum of about 40 mm. or less, and the cocks *H* and *F* are opened, the cock *B* being closed. The vessel connected at *K* is then partially exhausted, and, when the pressure has reached about 40 mm, the stop-cock *B* is opened, and the mercury is allowed to flow slowly from *A* to *C*. It falls into the fall-tube *CD*, as in an ordinary Sprengel pump, carrying with it the air from *C*. The vent-cock *D* is now opened carefully, and a quantity of air permitted to enter, sufficient to sweep the mercury rapidly up the return-tube *DA* into *A*. The end of this tube is curved downward, slightly, to diminish the spattering of the mercury. The vent-cock *D* requires no special mention. Any appliance for regulating the air-supply suffices, a thick-walled rubber tube, with pinch-cock, having been used with perfectly satisfactory results.

The operation of the pump is now perfectly continuous.[1] The mercury falls constantly from *C* into the fall-tube, and is as rapidly returned to *A*. A careful adjustment of *B* and *D* as the exhaustion advances gives a maximum efficiency.

The fall- and return-tubes should be 2.5 mm. inside diameter, as advised by Sprengel.[2]

With a pump of this description, after working for ten minutes, vacua so low that they could not be read on an ordinary manometer, were obtained, and electrical phenomena in tubes which had been exhausted gave evidence of extremely low pressures.

With suitable drying attachments, at *K*, *I*, and *D*, tubes for cathode ray experiments could undoubtedly be prepared.

The board supporting the pump may have a bracket on the back in the position shown by the dotted lines at *M*, which permits of its being firmly secured by means of a wood screw, to the edge of any bench or lecture table, while the small size and weight of the whole apparatus permits of its being freely moved from place to place.

The quantity of mercury required by the pump is very small, and, since it comes in contact with no rubber or grease, and is protected from dust, its contamination is entirely prevented.

The stop-cocks *B* and *F* are closed before the vessel connected with *K* is removed.

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[1] The cut shows the pump in operation.

[2] J. Chem. Soc., 1865, 15.

REVIEWS.

THE PRACTICAL METHODS OF ORGANIC CHEMISTRY. By LUDWIG GATTERMANN, PH.D. Translated by William B. Shober, Ph.D., Instructor in Organic Chemistry in the Lehigh University. New York: The Macmillan Company.

This book, which is a translation of Prof. Gattermann's valuable work is, in the words of the translator, "intended for those students of chemistry who have not yet become sufficiently familiar with scientific German to be able to read it accurately without constant reference to a dictionary." The first part of the book contains clear and detailed descriptions of the various operations necessary in connection with the preparation of organic compounds, and also the best methods for their analysis. The part devoted to organic preparations is somewhat similar to the works of Fischer and Levy on this subject; but it is more general in its nature. The translator has followed the methods of classification adopted by Prof. Gattermann and has reproduced the cuts of apparatus in the German edition. He has had the benefit of Prof. Gattermann's suggestions as to the correction of some inaccuracies in the German edition and has introduced a table to facilitate the calculation of nitrogen in organic analyses. The translation is excellent, and the book can be recommended as a valuable addition to the English works on organic preparations.

J. E. G.

NOTES ON QUALITATIVE ANALYSIS, arranged for the use of students of the Rensselaer Polytechnic Institute. By W. P. MASON, Professor of Chemistry. Third Edition. Easton, Pa.: Chemical Publishing Company. 1896. Price, 80 cents.

This manual differs from others written for the same purpose, in its brevity. So few reactions are given for each metal that the book seems available only for the most elementary instruction. The author even omits all methods for analysis of the phosphates of the alkaline earths as too difficult for beginners.

The other feature of this book is found in frequent references to chemical works and journals. It would seem that if a student is not ripe for a method of detecting aluminium in the presence of phosphates he would derive little benefit from dipping into chemical literature, but the author's experience has evidently led him to a different conclusion.

E. R.

CHEMISTRY FOR BEGINNERS. By EDWARD HART, Professor of Chemistry in Lafayette College. Third Edition, revised and greatly enlarged. Easton: Chemical Publishing Company. 1896. Price, $1.50.

The very worthy object which Dr. Hart had in mind in preparing this book was to provide the beginner with directions for a large number of experiments requiring but simple apparatus, and at the same time with a sufficiently detailed statement of elementary chemical phenomena to serve for a "beginner's course."

The experiments, which number about 220, are in the main well chosen. The chief adverse criticism to be passed upon them is that the author in his desire to be concise has, at least in many cases, given too little space to the discussion of the method of procedure and of the point to be illustrated. It is poor economy to cut down this portion of a book intended for beginners, since it at once throws a greater burden upon the instructor, and generally results in ignorance on the part of the student as to the object for which the work is done, even when the experiment in question is, ordinarily speaking, successful.

The descriptive portion of the book has apparently been carefully brought up to date. Modern commercial methods for the preparation of chemical substances are, as a rule, clearly and concisely described. The commercial application of many chemical products is treated in an especially satisfactory way. But far too many compounds are mentioned—they can hardly be said to be described—for a student to be able to consider with profit at the beginning of his course. This is especially true of that portion of the book devoted to carbon compounds: a distinct lack of proportion may be said to characterize the work from this point of view.

Of the method of handling the theoretical side of the subject, much less can be said in commendation. The beginner is confronted at the outset with theoretical points for which he has had no suitable preparation. As a single instance, he is told in Chapter III. that the difference between oxygen and ozone is supposed to lie in the fact that their molecules contain two and three atoms, respectively, and that their symbols are O_2 and O_3; whereas no explanation of atoms, molecules, symbols, etc. is given for several chapters. Again, many equations are given as explanatory of certain general phenomena, which do not represent actual reactions. Thus, as showing the production of hydrogen by substitution is cited the action of silver, lead, copper, bismuth, and chromium—among other metals—upon nitric acid.

Finally, statements constantly appear which should not have been made without qualification; in these cases also the author's conciseness results in inaccuracy. For example, we are told that "the modern theory of chemistry is due to Lavoisier;" that "life is a process of oxidation in which food is the fuel and carbon dioxide is thrown off to mix with the air;" that "when carbonic acid is acted upon by a metal which replaces one atom of hydrogen, such as sodium, we get first a carbonate containing one hydrogen atom, thus $NaHCO_3$. If two atoms of sodium act upon carbonic acid both hydrogen atoms are replaced and we have Na_2CO_3."

W. W. R.

MANUAL OF DETERMINATIVE MINERALOGY, with an introduction on Blowpipe Analysis. By GEORGE J. BRUSH, Director of the Sheffield Scientific School of Yale University. Revised by SAMUEL L. PENFIELD, Professor of Mineralogy in the Sheffield Scientific School of Yale University. New York: John Wiley & Sons. 1896. Price, $3.50.

Prof. Brush's book is so favorably known that it needs no praise; suffice it to say that Prof. Penfield has thoroughly revised the first half of the book, introducing new methods, and prescribing the methods incidental to the tests for the elements in detail. A revision of the tables for the determination of minerals is promised for a future edition. In the present edition half of the book is made up of these tables taken from a former edition by Prof. Brush. It is to be regretted that the publisher did not print the tables in good type; they are printed from worn out plates, and partially illegible words or letters can be noted on every page.

E. R.

CHEMISTRY IN DAILY LIFE. Popular Lectures by DR. LASSAR-COHN, Professor in the University of Königsberg. Translated by M. M. PATTISON MUIR, M.A. London and Philadelphia: J. B. Lippincott Co. Price, $1.75.

These lectures treat of many subjects. The air, combustion, flame, illuminants, plant life and agriculture, foods, explosives, tanning, dyes, potash, soda, soaps, glass, ceramics, photography, the metals and alkaloids are the principal ones. Professor Lassar-Cohn has succeeded in writing a book which is simple and clear enough to be understood by any person of intelligence, and yet the book is scientific in spirit and up to date in detail. It should be of particular value and interest to college students who have heard a course of lectures on chemistry, partly as a review, partly as emphasizing the practical applications of reactions and principles with which they are familiar.

E. R.

HANDBOOK FOR THE BIO-CHEMICAL LABORATORY, including Methods of Preparation and Numerous Tests Arranged Alphabetically. BY JOHN A. MANDEL, Professor of Chemistry at the New York College of Veterinary Surgeons, and Assistant to the Chair of Chemistry, etc., at the Bellevue Hospital Medical College and the College of the City of New York. First Edition. 101 pp. New York: John Wiley & Sons. London: Chapman & Hall.

This small handbook, designed principally for students, is divided into two parts. Part first, consisting of 61 pages, gives concise and accurate methods (in some cases more than one) for preparing the most important substances found in the tissues and fluids of the animal body; in some instances methods for the synthetic preparation of these substances are also given. The author does not claim originality in any of these methods, and states in his introduction that the methods have been taken from the most recent, important works on physiological chemistry. Either the empirical or structural formula is given with the name of the substance isolated. It seems to the writer of this notice that in a book of this kind, designed for students, it would have been well to introduce chemical equations wherever practicable, or to introduce interrogation marks after certain directions, thus bringing these points to the attention of the student. Otherwise the manipulations are mechanical and the directions are equivalent to so many receipts in a cook-book.

Part second, consisting of 40 pages, is taken up with some 200 well-known tests used in bio-chemical and physiological chemical work. These are arranged in alphabetical order, and the name of the person who suggested the test, or the name under which it is ordinarily known is given in each case. Such a list has long been desired by workers in this field; and it is an important addition to bio-chemical laboratory literature.

The value of the book lies in its compactness. It gives students in a few pages all the data really necessary for immediate work, and thus saves time which would be used in searching for methods and tests in larger works. T. B. A.

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VOL. XIX. FEBRUARY, 1897. NO. 2.

AMERICAN

CHEMICAL JOURNAL.

A CONTRIBUTION TO THE STUDY OF WATER SOLUTIONS OF SOME OF THE ALUMS.[1]

BY HARRY C. JONES AND E. MACKAY.

Introduction.

When a solution of a mixture of two salts having a common ion is subjected to crystallization, the two salts may either crystallize out separately or crystals may form containing both. In the latter case two modes of separation are to be distinguished, according as the crystals formed are of variable or of constant composition. When of variable composition they are mixed crystals, or isomorphous mixtures. When the constituent salts are present in constant molecular proportions, the crystalline compound is a double salt. The constancy of the composition of the crystals of a double salt raises the question whether the double salt is present as such in solution or is formed only at the moment of crystallization.

The question of the existence of double salts in solution has attracted the attention of many investigators, and a variety of methods have been used in obtaining light upon it. The most important of these are grouped according as they have to do with (a) the diffusion, (b) the thermal changes, (c) the volume changes, (d) the solubility, (e) the electrical properties, or (f) the cryoscopic behavior of solutions of the compounds investigated.

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[1] From the dissertation of E. Mackay, Johns Hopkins University, June, 1896.

Diffusion.

Graham,[1] in his classical researches on diffusion, studied incidentally the diffusion of a few double salts, among them being ordinary alum and the double sulphate of magnesium and potassium. He found that the constituents of the former were present in the diffused liquid in a proportion different from that in the alum itself, and inferred that the alum was at least partially decomposed in water solution. Graham found that the amount of the second double salt which diffused over was equal to the sum of the amounts of its constituents which diffused, when taken separately. He concluded that this double salt was not decomposed in solution.

Since Graham did not determine the proportion in which the constituents of the double sulphate of magnesium and potassium had diffused, but only the total amount diffused, his work was repeated by Marignac,[2] who, from an extensive series of observations, concluded that there is no difference in diffusion between mixtures of salts capable of forming double salts and those in which no union can take place. He inferred that double salts are formed only at the moment of crystallization.

The work of van der Wal,[3] who studied the diffusion of alums and other double sulphates, and of Ingenhoes,[4] who investigated barium acetonitrate and similar salts, lead to the same result. The latter found that the constituents of the salts examined diffused not in the proportion in which they existed in the double salt, but nearly as if they diffused separately. Rüdorff,[5] following the same mode of investigation, divided double salts into two classes according as the constituents were found in the diffusate in the same proportion as in the double salt, or in a different proportion. Rüdorff also investigated the relation between decomposition and concentration and found that, until near the point of saturation, the two were independent ; but if crystals of the double salt were placed upon the diaphragm so as to maintain saturation, the proportion in which the constituents diffused approached much more nearly their proportion in the double salt. He concluded that molecular compounds exist in fully saturated solutions.

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[1] Phil. Trans., Lond., 1850, 1.

[2] Ann. chim. phys., [5], **2**, 546.

[3] Inaugural Dissertation, Leyden, 1869.

[4] Ber. d. chem. Ges., **12**, 1678.

[5] *Ibid*, **21**, 4, 1882, 3044; **23**, 1846.

This conclusion was criticised by Ostwald[1] and later by Trevor[2] on the ground that the effect observed was due to the more rapidly diffusing constituent becoming relatively less concentrated in the diffusion vessel. The latter undertook a series of experiments, the result of which was to confirm this view.

On the other hand, E. Fischer and Schmidner[3] allowed a saturated solution of ferrous ammonium sulphate to diffuse upwards through rolls of filter paper inside of a glass tube, and found that the proportion of the constituents in the filter paper was the same as in the double salt.

Thermal Changes.

Thermal data, in so far as they lead to a conclusion in reference to the existence of double salts in solution, are summarized thus by Berthelot.[4] "Everything indicates that double salts formed with a *feeble* disengagement of heat are to be regarded as separated in greater part into their constituents, by water." Favre and Valson,[5] on finding that the constituents of the alums evolved no heat on mixing, concluded, as would Berthelot, that the latter came into existence only through crystallization.

Graham[6] had previously made similar experiments with other double sulphates, and had reached the same conclusion. He found, on the other hand, that thermal changes occurred when solutions of the chlorides of mercury and ammonium were mixed. Berthelot[7] observed in general that the thermal changes produced by mixing solutions of the halogen salts of mercury and potassium were not equal to the sum of the thermal changes for the component salts, and concluded that the existence of double salts in such solutions was thereby proven.

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[1] Ztschr. phys. Chem., **3**, 601.

[2] *Ibid*, **7**, 468.

[3] Ann. Chem. (Liebig), **272**, 156.

[4] Méc. Chem., II, 324.

[5] Compt. rend., **74**, 1165.

[6] Phil. Mag., **20**, 539; **24**, 401.

[7] Ann. chim. phys. [5], **29**, 198.

Volume Changes.

Chemical changes being accompanied by volume change, the latter is often used as an index to the former. Kremers,[1] finding no change of volume on mixing solutions of salts capable of forming double salts, inferred that double salts are incapable of existence in water solution. A similar conclusion was drawn by Favre and Valson,[2] based on the fact that the density of a solution of potassium cupric sulphate is the mean of the densities of its constituents.

Gerlach,[3] however, noticed a slight contraction in volume on mixing solutions of the constituents of the alums. This became more marked as the concentration of the solutions increased. Upon this and other grounds he was led to the belief that these double salts exist as such in solutions. The conclusions of Groshans[4] from observations on double chlorides and sulphates confirmed those of Kremers.

Solubility of Salt Mixtures.

Researches upon the solubility of salt mixtures, especially upon the conditions of equilibrium in solution, when two salts capable of forming a double salt are dissolved together, have contributed to our knowledge of the existence of double salts in solution. From the work of Kopp[5] and others, extended by his own investigations, Mulder[6] drew the conclusion that well defined double salts exist in saturated solutions of salt mixtures. This conclusion was based upon the observation that in such solutions, saturated with respect to each component, the salts are often found in simple molecular proportions. Some work of Rüdorff[7] seemed to point to a different conclusion, but this has been interpreted otherwise by Trevor. The studies of equilibrium of Ditte[8] on the double iodide of lead and potassium ($PbI_2.K_2I_2.nH_2O$), of Roozeboom[1] on astrakanite, of Meyerhoffer,[2] Vriens,[3] Schreinemaker,[4] and van der Heide[5] have led to the general result that there are certain limits of temperature, outside of which double salts are capable of existing in their solutions.

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[1] Ann. der Phys. Pogg., **98**, 58.

[2] Compt. rend., **77**, 907.

[3] Ztschr. anal. Chem., **28**, 485.

[4] Des Dissolutions Aqueuses, 2–7.

[5] Ann. Chem. (Liebig), **34**, 260.

[6] Jsb. Chem., 1864, 92; 1866, 65.

[7] Ann. der Phys. Pogg., **148**, 558.

[8] Ann. chim. phys., [5], **24**, 226.

From van't Hoff's application of the gas laws to solution, Nernst[6] deduced theoretically and quantitatively what had been already qualitatively established by experiment, that if to a saturated solution of a salt, a solution of another salt having a common ion, be added, the solubility of the first salt is decreased and a part of it precipitated. On examining certain cases in which the solubility of the first salt is increased under the conditions named above, Le Blanc and Noyes[7] succeeded in showing that the apparent exceptions were due to the formation of double salts in solution. Rose[8] attributed to the same cause those cases in which a salt is found to be more soluble in the solution of another salt than in water. The view that the solution of silver chloride in ammonia is accompanied by the formation of a double salt in the solution has been confirmed by Bodländer.[9]

Electrolysis.

The application of electrolysis to the study of the condition of double salts was made early in the present century by Parret,[10] who found that when potassium ferrocyanide was electrolyzed, alkali appeared at the negative pole while oxide of iron and prussic acid appeared at the positive. The work of Daniell and Miller[11] on the same salt, extended by Hittorf[12] to many other double salts, led to the view that double salts are of two classes ; those which do not exist as such in solution, and those containing a metal combined with a complex radical, which are capable of existing in water solution, undecomposed. In the nomenclature which Ostwald[13] proposed the latter are called "complex salts;" the term "double salt" being applied to members of the first class only. To the complex salts he refers potassium ferrocyanide and analogous compounds. The alums are classed as double salts. Between these extreme types varying degrees of decomposition of the complex molecules may exist in solution.

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[1] Ztschr. phys. Chem., **2**, 513.

[2] *Ibid*, **3**, 336.

[3] *Ibid*, **7**, 194.

[4] *Ibid*, **9**, 57.

[5] *Ibid*, **12**, 416.

[6] *Ibid*, **4**, 372.

[7] *Ibid*, **6**, 385.

[8] Ann. der. Phys. Pogg., **82**, 545.

[9] Ztschr. phys. Chem., **9**, 730.

[10] Phil. Trans. Lond., 1814, 527.

[11] Ann. der Phys. Pogg., **64**, 18.

[12] *Ibid*, **106**, 513.

[13] Ztschr. phys. Chem., **3**, 596.

Electrical Conductivity.

Researches upon the electrical conductivity of double salts and salt mixtures are numerous. Of chief importance in the present connection are those of Bouchotte[1] and Paalzow[2] on the sulphates of copper and zinc in common solution; of Svenson[3] on the alums, of Grotrian[4] on potassium cadmium iodide (K_2CdI_4) of Freund,[5] Bender,[6] Bouty,[7] Arrhenius,[8] and Chroustchoff and Packhoff[9], on mixtures of electrolytes; of Klein[10] on mixtures and double salts; of Wershoven[11] on dilute solutions of cadmium salts; and of Kistiakowsky[12] on dilute solutions of complex salts. The results of these investigations, in so far as they refer to the dissociation of double salts, agree in showing that with increasing dilution many double salts rapidly approach the condition of a simple mixture. Klein, who compared the conductivities of salt mixtures capable of forming double salts, with the conductivities of those whose constituents could not combine, showed that in the former case the difference between the conductivity of the mixture and the mean conductivity of its constituents was much greater than in the latter, for concentrated solutions. He inferred that in concentrated solutions of double salts there is only a partial breaking down of the complex molecules into their constituents. Kistiakowsky found that even in very dilute solutions of complex salts the complex ions remained undecomposed. The conductivity method has also been applied by Le Blanc and Noyes, by Bodländer, and others to the problem of the existence of double salts in solution, with the result that in certain cases the existence of such is indicated as probable.

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[1] Compt. rend., **62**, 955.

[2] Ann. der Phys. Pogg., **136**, 489.

[3] Ann. der Phys. Beibl, **2**, 46; Inaug. Dissertation, Lund.

[4] Ann. der Phys. Wied, **18**, 177.

[5] *Ibid*, **7**, 44.

[6] *Ibid*, **22**, 179.

[7] Ann. chim. phys. [6], **3**, 433; **14**, 74.

[8] Ann. der Phys. Beibl, **9**, 437; Ann. der phys. Wied., **30**, 51.

[9] Compt. rend., **108**, 1162.

[10] Ann. der Phys. Wied., **27**, 151.

[11] Ztschr. phys. Chem., **5**, 481.

[12] *Ibid*, **6**, 97.

Lowering of the Freezing-point.

The application of the freezing-point method to the problem in question has been made, especially by Raoult.[1] By comparing the lowering caused by double salts with the sum of the lowerings of their constituents, he concluded that certain double sulphates, including the alums, are entirely decomposed into the simpler sulphates, when dissolved in water; while certain other double salts undergo only partial decomposition under the same conditions.

The foregoing summary of our knowledge with respect to the existence of double salts in solution, will show that the classification of such salts into two groups according as they are wholly or but partially decomposed by water, is well established so far as dilute solutions are concerned, but that in more concentrated solutions the evidence is not yet sufficient to regard the classification as satisfactory.

The present investigation was undertaken with the object of obtaining such further data as might justify more definite conclusions. The work thus far has been devoted mainly to the alums, as representatives of that extreme type of double salts which were supposed by some to be completely broken down in water solution. It has already been extended to one of the double chlorides, but since much more work will be necessary along this line before justifiable conclusions can be drawn, the results now in hand will be supplemented before they are published.

The conclusions reached in this paper with respect to the existence of the alums in solution, are based upon a comparison of the electrical conductivity and cryoscopic behavior of the double salts, with that of their constituent salts, with a view to determine to what extent the solutions of the double salts correspond to mixtures. Since the double sulphates correspond in general to one of the two types:

$$\text{I.}\quad R'_2SO_4 + R''SO_4 + 6H_2O.$$
$$\text{II.}\quad R'_2SO_4 + R'''_2(SO_4)_3 + 24H_2O,$$

any conclusions reached with respect to the alums in solution, would probably apply directly to a larger group of the double sulphates.

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[1] Compt. rend., 99, 914.

The measurements of the conductivity of the solutions were made by the Kohlrausch method. The special form of the apparatus employed was that described by Ostwald.[1] The bridge wire was calibrated by the method of Strouhal and Barus.[2] Two resistance cells, with electrodes at different distances, were used—one for solutions more concentrated than 0.001 normal, the other for solutions more dilute. In this way satisfactory tone-minima were obtained throughout a wide range of dilution. The temperature selected for the measurements was in general 25°. By means of a thermostat the temperature was easily maintained constant to within one-tenth of a degree.

The flasks and pipettes used in making up the solutions were calibrated by the method of Morse and Blalock.[3] The solutions were standardized by the determination of some constituent, in a measured volume. In a few cases the nature of the salt allowed it to be weighed directly.

Since the conductivity of the water affects very considerably the conductivity of the more dilute solutions, all the water used was purified as follows: Ordinary distilled water was treated with potassium permanganate and a little sulphuric acid, and the vapor from this solution passed into distilled water containing permanganate and a little potassium or sodium hydroxide. The vapor from the second solution was condensed in a tube of block-tin. The apparatus used for purifying the water was found to be so efficient that it is sketched in some detail in Fig. I.

A is a balloon flask, preferably of Jena glass, holding from five to six liters. *B* is a tubulated retort of about four liters capacity. The two are connected by a glass tube of about 1 cm. diameter, bent as shown in the drawing. Where the tube enters the retort at *H* it is tightly wrapped with thin asbestos paper, forming a steam-tight joint. The use of a cork in contact with the steam in the retort is thus avoided. Into the neck of the retort, at *C*, is fitted an adapter, bent as shown in the drawing, and partly filled with glass wool, *W*. The joint is made secure by wrapping the end of the adapter with asbestos paper. The small end of the adapter projects well into the tin condenser *D*, which is surrounded by the cooling jacket *F*. *E* is a carefully cleaned flask, which receives the water from the condenser.

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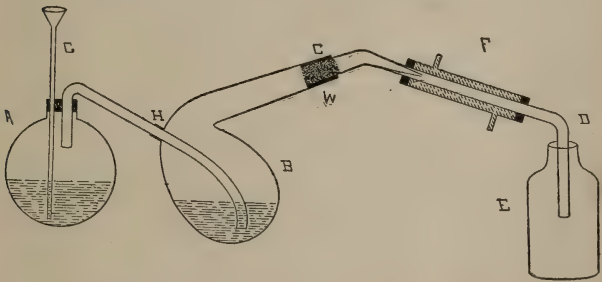
[1] Ztschr. phys. Chem., **2**, 561.

[2] Ann. der Phys. Wied., **10**, 326.

[3] This JOURNAL, **16**, 479

Ordinary distilled water is introduced into the vessel *A*, together with a little sulphuric acid and potassium permanganate, through the funnel tube *G*. It is heated to boiling, the vapor passing into *B*, which contains distilled water, potassium permanganate, and a little potassium or sodium hydroxide. A small flame is sufficient to keep the liquid in *B* at the boiling temperature. The vapor passes from *B* along the long neck of the retort, over the glass wool, which is meant to arrest any trace of permanganate carried along by the steam, into the tin condenser, and is received in the flask *E*. Certain precautions must be taken in fitting up and using the apparatus. The glass wool, *W*, introduced into the adapter arm, *C*, must fill only the lower part of the arm, otherwise there is danger that a trace of alkali will dissolve from it and be swept over into the condenser. The glass wool used should be washed well with dilute hydrochloric acid and heated for a long time in a current of water vapor. Whenever the apparatus is cleaned and refilled, which should be done about once a week when in constant use, the distillate collected at first must be discarded, since it always contains a trace of alkali, probably of

FIG. 1



ammonia, formed by the action of the alkaline permanganate on the ordinary distilled water introduced into B. When this is once removed there is no further escape of ammonia possible, since the organic impurities in the water are destroyed by the permanganic acid in A, and the ammonia combines with the sulphuric acid present in that vessel. The carbon dioxide liberated in A is absorbed by the alkali in B. The process is thus perfectly continuous for at least a week, or it can be interrupted at any time by removing the burners. Four to five liters of water were obtained daily from this apparatus.

The water purified by this method gave a conductivity at 25° varying from 1.5 to 2×10^{-6} mercury units. The conductivity of the water used was measured for each series of determinations and the corresponding correction applied. In making a series of conductivity measurements, the general method adopted was to make up from the original solution, standardized by analysis, a solution which was a simple multiple or fraction of normal. Twenty-five or fifty cc. of this solution were then measured with a pipette into the cell and successive dilutions prepared from this in the cell itself, by withdrawal of a measured portion and addition of an equal volume of water. As a check upon errors of dilution, a series of solutions were made up directly in measuring flasks at intervals corresponding to several of the dilutions in the cell. These solutions were used as standards of conductivity, and when the conductivity of the cell dilution differed appreciably from the standard, a proportional correction was applied to the former, in the manner indicated by Kohlrausch.[1] When this correction exceeded one-half of 1 per cent. the measurements were repeated. The cell was standardized at frequent intervals with a one-fiftieth normal solution of potassium chloride, which had been recrystallized five times. In certain cases in which the solutions were found to be unstable at great dilutions, the check solutions were made up immediately before measuring their conductivity.

A Method for Titrating Aluminium.

The necessity of standardizing solutions containing aluminium occurred so often in the progress of the work, that a reliable and convenient method of determining this element by titration was highly desirable. None of the methods described in the literature seem to have proved satisfactory. That of Baeyer[1], by the titration of sodium aluminate with sulphuric acid, using litmus and methyl orange as indicators, is described as a tedious and uncertain process, while in the method of Lunge[2] the ratio of the acid consumed to the aluminium has been the subject of much discussion.

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[1] Ann. der Phys. Wied., **26**, 184.

After an unsuccessful attempt to titrate aluminum in the alum by means of a solution of barium hydroxide, the following method was devised. It gave, however, only fairly satisfactory results. A measured volume of the alum solution was heated nearly to boiling and all the sulphuric acid precipitated with barium chloride. Care should be taken to use only a small excess of the latter. A few drops of litmus were added and a one-twentieth normal solution of ammonia run in slowly and with constant shaking until the litmus showed a weakly alkaline reaction. A large excess of ammonia must be avoided, since it would dissolve to some extent the precipitated aluminium hydroxide. The change in the color of the litmus on adding the ammonia was gradual, and thus the aluminium could not be directly titrated with ammonia with any approach to accuracy, as we convinced ourselves by repeated trial. The solution containing the barium sulphate and aluminium hydroxide as precipitates, was diluted to a known volume and allowed to stand some hours until most of the precipitate had settled. It was found convenient to carry out the entire analysis in measuring flasks holding 100 cc. After the precipitate had settled a part of the solution was decanted and passed through a small filter paper, the first part of the filtrate being discarded to avoid change in the concentration of the ammonia by the filter paper. To 50 cc. of the filtrate a few drops of litmus were again added and the solution again titrated to color with standard hydrochloric acid. The second addition of the litmus is necessary, since the aluminium hydroxide acts as a mordant with the dye and removes almost completely that which was added at first.

[1] Ztschr. anal. Chem., **24**, 542; **25**, 183.

[2] Ztschr. angew. Chem., **227**, 293.

A solution of potassium aluminium alum titrated by this method gave the following results :

Determinations.

I.	1 cc. solution contains	0.0948	gram alum.
II.	1 cc. " "	0.0946	" "
III.	1 cc. " "	0.0945	" "
IV.	1 cc. " "	0.0944	" "
V.	1 cc. " "	0.0944	" "
	Mean	0.0945	" "

The result of the gravimetric analysis of this solution by precipitating the sulphuric acid with barium chloride gave 0.09486 gram alum in 1 cc.

The Conductivity Results.

The conclusions drawn from the conductivity results are based upon a comparison of the conductivity of the constituents of the alum, with the conductivity of the alum itself, under the same conditions, as has been stated. On examining the literature, we found that very few conductivity determinations of sufficiently concentrated solutions of the constituents of the alums had been made at 25°, and the temperature coefficients given were scarcely accurate enough for our purpose. Measurements of the conductivity of a number of solutions of potassium sulphate, aluminium sulphate, and chromium sulphate at 25° were therefore made.

Potassium Sulphate.

The salt, purified by repeated crystallization, was dried to constant weight in an air-bath, and solutions were prepared from a weighed amount of the dry salt.

In the following tables the conductivities are expressed as "molecular conductivities," as defined by Ostwald[1] instead of in "equivalent molecular" units, in order to facilitate the comparison of the conductivities of solutions containing equal numbers of gram-molecules per liter, but of different concentration if expressed as equivalent normal.

The symbols $\mu_v 15°$ and $\mu_v 25°$ denote respectively the molecular conductivities at 15° and 25°.

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[1] Lehrb. d. allg. Chem., II, 621.

Table I.

K_2SO_4 [174.34.]

Gram-molecules per liter.	Volume.	$\mu_v 15^\circ$.	$\mu_v 25^\circ$.
0.333	3.0	....	157.4
0.250	4.0	134.7	167.9
0.2175	4.6052	....	170.2
0.10855	9.2104	....	186.9
0.1	10.0	148.2	187.0
0.05427	18.4208	....	202.8
0.5	20.0	162.9	205.1
0.0333	30.0	167.2	213.9
0.025	40.0	171.7	220.3
0.01666	60.0	179.4	229.1
0.005	200.0	200.7	252.4
0.0025	400.0	....	262.2
0.0005	2000.0	....	276.5
0.00025	4000.0	....	281.9
0.00005	20000.0	237.8	279.6

The only direct measurements of the conductivity of solutions of potassium sulphate, at 25°, available for comparison with our own, were those of Walden,[1] which, on interpolation gave values which agreed fairly well with our own, as can be seen by comparing Table II with Table I.

Table II.

Walden's Results for Potassium Sulphate.

Volume.	$\mu_v 25^\circ$.
64	232.2
128	246.0
256	256.8
512	265.4
1024	272.8
2048	278.6

Aluminium Sulphate.

The so-called chemically pure aluminium sulphate was found to contain a large quantity of sodium which was difficult to remove, so that it was decided to prepare the salt from a pure aluminium compound. Perfectly pure potassium aluminium alum prepared by repeated crystallization was treated with ammonia, which precipitated the aluminium as the hydroxide. The precipitate was then washed until it was found to be free from ammonia and potassium; this operation requiring several weeks. The washing was effected by boiling the precipitate with a large volume of water, for some time, allowing it to settle, and successively decanting and filtering. While the precipitate was on the filter, it was washed many times with boiling water. The hydroxide was then brought into a large beaker, treated with several liters of water and again boiled for a considerable time. This treatment was repeated from fifteen to twenty times, when a pure specimen of aluminium hydroxide was obtained. The pure hydroxide was dissolved in sulphuric acid, using a slight excess, as indicated by methyl orange, to prevent the formation of basic aluminium sulphates. The excess of acid was removed by dissolving the salt in water and precipitating it several times by adding alcohol.

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[1] Ztschr. phys. Chem., 2, 49.

The last traces of alcohol were removed by warming the salt gently in an air-bath. The aluminium sulphate thus obtained was a beautiful white powder. A qualitative analysis showed that it contained neither potassium nor ammonium. In a sample chosen, both the sulphuric acid and the aluminium were determined, with the result that they differed from the calculated equivalents well within the error of experiment. A solution of the salt was prepared, and standardized by determining the amount of sulphuric acid in a measured volume.

Determination.

I. $Al_2(SO_4)_3$ per cc. = 0.04470 gram.
II. " " " = 0.04478 "

Mean = 0.04474 "

The amount of the aluminium sulphate present in the solution was therefore equivalent to 0.1307 gram-molecules per liter.

In the following table of conductivity measurements of aluminium sulphate, it will be seen that two series, more or less complete, were carried out at 25°.

Table III.

$Al_2(SO_4)_3$ 342.34.

Gram-molecules per liter.	Volume.	$\mu_v 15^\circ$.	I. $\mu_v 25^\circ$.	II. $\mu_v 25^\circ$.	Mean $\mu_v 25^\circ$.
0.21715	4.6052	....	105.7	....	105.7
0.10855	9.210	107.7	130.3	....	130.3
0.06666	15.0	....	148.2	148.5	148.3
0.05427	18.4208	....	153.6	....	153.6
0.03333	30.0	139.1	172.5	172.7	172.6
0.016666	60.0	....	202.3	202.1	202.2
0.003333	300.0	243.6	300.4	300.8	300.6
0.001666	600.0	....	359.5	358.6	359.0
0.0005	1999.9	382.4	....	....	....
0.0003333	3000.0	....	530.0	531.7	530.8
0.00025	4000.0	447.4	....	....	....
0.0001666	6000.0	....	611.6	611.4	611.5
0.00003333	30000.0	....	806.1	809.1	807.6
0.000025	40000.0	678.4	....	....	....
0.0000166	60000.0	....	869.4	869.4	869.4
0.0000125	80000.0	708.7	....	....	....
0.00000625	160000.0	715.2	....	....	....

These results agree satisfactorily with some measurements of dilute solutions by Walden at the same temperature.

Chromium Sulphate.

The salt was prepared under the direction of Prof. Renouf of this laboratory, by reducing chromic acid with ether, under a bell jar, according to the method described in his "Inorganic Preparations," p. 78.

A very concentrated solution of the compound was made. In order to diminish the error of analysis, the solution standardized, was prepared from the original by diluting one volume to twenty.

Determination I. $Cr_2(SO_4)_3$ in 1 cc = 0.007426 gram.
" II. " " " " = 0.007410 "

Mean = 0.007418 "

Hence the original solution contained 0.3779 gram-molecules per liter.

The conductivity results for chromium sulphate are given in Table IV.

Table IV.

$Cr_2(SO_4)_3 = 392.58$.

Gram-molecules per liter.	Volume.	$\mu_v 15°$.	$\mu_v 25°$.
0.333	3	....	94.2
0.250	4	86.2	107.3
0.100	10	....	139.0
0.05	20	132.3	162.7
0.025	40	....	190.7
0.005	200	233.2	288.2
0.0025	400	....	346.5
0.0005	2000	....	558.2
0.00025	4000	....	671.2

The conductivity values found for chromium sulphate by Walden[1] differ widely from the above. A comparison of a few dilutions will show the extent of the difference. In Table V, column I, are Walden's values reduced to molecular conductivity units, column II our values, obtained by interpolation in the above results.

Table V.

Comparison of Results for Chromium Sulphate.

Volume.	I. $\mu_v 25°$.	II. $\mu_v 25°$.
192	378.0	283.4
384	439.2	342.0
1536	589.2	497.0
3072	669.6	617.0

The values of Walden are throughout much higher than our own. If the mean be taken of Walden's values for chromium sulphate and the values for the corresponding solutions of potassium sulphate, it would lead one to expect conductivity results for potassium chrome alum far larger than those found; since it is known that the conductivity of an alum is somewhere near the mean of the conductivity of its constituents. However, on account of this discrepancy, we propose to repeat the conductivity measurements with a new preparation of the chromium sulphate. Having determined the conductivity of these constituents of the alums, that of the alums themselves was next measured.

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[1] Ztschr. phys. Chem., 1, 541.

Potassium Aluminium Alum.

The alum was purified by repeated crystallization and was found to be free from iron, sodium and ammonium, which might be present as impurities. The flame reaction was that of a clean potassium salt. A solution was prepared, approximately saturated at 20°, and was standardized by precipitating the sulphuric acid with barium chloride. The mean of three determinations gave $KAl(SO_4)_2 + 12H_2O$ in 1 cc. = 0.09486 grams, which is equivalent to 0.19995 gram-molecules per liter. The conductivity results are incorporated in Table VI.

Table VI.

$KAl(SO_4)_2 + 12H_2O = 474.41$.

Gram-molecules per liter.	Volume.	I. $\mu_v 25°$.	II. $\mu_v 25°$.	Mean of I and II.
0.19995	5.0012	133.9	133.9	133.9
0.125	8.0	149.2	149.2	149.2
0.05	20.0	178.3	178.3	178.3
0.025	40.0	202.5	202.5	202.5
0.005	200.0	268.2	269.9	269.0
0.0025	400.0	304.2	306.3	305.2
0.0005	2000.0	407.0	406.8	406.9
0.00025	4000.0	468.2	466.8	467.5

Sodium Aluminium Alum.

The alum was prepared by dissolving together equivalent quantities of sodium and aluminium sulphates so as to form a concentrated solution, placing this solution in a tall narrow glass cylinder and pouring on the water solution a thick layer of alcohol. This was allowed to stand for some time with the expectation that the alcohol would diffuse through the liquid below, causing the alum, which was very soluble in water, to crystallize out. This was found to require so much time that the process was hastened by jarring the cylinder occasionally. In the course of a few weeks, large crystals of sodium alum were formed, but with these were mixed a few crystals of some other salt, also soluble in alcohol with difficulty. When the mixture was treated quickly with a little cold water, the impurity readily dissolved, leaving the alum crystals entirely free from any foreign matter, as could be verified under a microscope. The crystals were powdered and dried for a long time, to remove all traces of alcohol. A solution was prepared and standardized by gravimetric determinations of sulphuric acid.

Determination I, $NaAl(SO_4)_2 12H_2O$ in 1 cc. = 0.02402 gram
" II, " " 1 " = 0.02407 "

Mean = 0.02404 "

The conductivity results are given in Table VII.

Table VII.

$NaAl(SO_4)_2 + 12H_2O = 458.33.$

Gram-molecules per liter.	Volume.	I. $\mu_v 25°$.	II. $\mu_v 25°$.	Mean.
0.05	20.0	161.5	161.6	161.6
0.025	40.0	184.4	184.7	184.6
0.005	200.0	250.0	251.2	250.6
0.0025	400.0	286.7	284.2	285.4
0.0005	2000.0	380.0	378.8	379.5
0.00025	4000.0	435.5	435.2	435.4

Ammonium Aluminium Alum.

The salt, after eleven crystallizations, was found to be free from sodium, but still contained a trace of potassium. A solution was standardized by titrating the aluminium.

Determination.

I. $NH_4Al(SO_4)_2 + 12H_2O$ in 1 cc. = 0.04550 gram.
II. " " 1 " = 0.04585 "

Mean = 0.045675 "

The solution contained therefore 0.10076 gram-molecules. The conductivity results are given in table VIII.

Table VIII.

$NH_4Al(SO_4)_2 + 12H_2O = 458.33.$

Gram-molecules per liter.	Volume.	I. $\mu_v 25°$.	II. $\mu_v 25°$.	Mean.
0.1	10.0	152.8	152.9	152.8
0.05	20.0	174.5	175.0	174.8
0.025	40.0	198.1	198.4	198.2
0.005	200.0	261.4	260.6	261.0
0.0025	400.0	297.1	294.9	296.0
0.0005	2000.0	390.0	389.2	389.6
0.00025	4000.0	452.4	452.4	452.4
0.00005	20000.0	568.4	560.0	564.2
0.000025	40000.0	608.4	602.8	605.6

Potassium Chrome Alum.

The salt, purified by repeated crystallization from water at 35°, was dissolved, and the solution standardized by precipitating the sulphuric acid as barium sulphate.

The analysis gave :

I. 0.11742 gram $KCr(SO_4)_2 + 12H_2O$ per cc.
II. 0.11846 " " " "

Mean 0.11744 gram chrome alum per cc. This is equivalent to 0.2351 gram-molecules per liter.

In the following table are incorporated the results of the measurements of conductivity of the solutions :

Table IX.

$KCr(SO_4)_2 + 12H_2O = 499.53.$

Gram-molecules per liter.	Volume.	I. $\mu_v 25°$.	II. $\mu_v 25°$.	Mean.
0.1	10.0	147.8	148.1	147.9
0.05	20.0	170.5	170.3	170.4
0.025	40.0	195.4	195.0	195.2
0.005	200.0	266.7	266.5	266.6
0.0025	400.0	306.1	304.9	305.5
0.0005	2000.0	418.6	418.8	418.7
0.00025	4000.0	472.4	471.6	472.0

Ammonium Chrome Alum.

The salt was purified as in the case of potassium chrome alum, the solution prepared and standardized in the same manner. The result of the analysis was :

I. 1 cc. of solution contained 0.09266 gram $NH_4Cr(SO_4)_2 + 12H_2O$.

II. 1 cc. of solution contained 0.09282 gram $NH_4Cr(SO_4)_2 + 12H_2O$.

Mean = 0.09274 gram, which corresponded to 0.194 gram-molecules per liter. The conductivity results are given in Table X.

Table X.

$NH_4Cr(SO_4)_2 + 12H_2O = 478.44.$

Gram-molecules per liter.	Volume.	I. $\mu_v 25^\circ$.	II. $\mu_v 25^\circ$.	Mean.
0.1	10.0	145.4	144.7	145.0
0.05	20.0	167.2	167.1	167.1
0.025	40.0	191.5	191.1	191.3
0.005	200.0	263.8	263.6	263.7
0.0025	400.0	304.0	303.6	303.8
0.0005	2000.0	....	415.3	415.3
0.00025	4000.0	484.6	477.5	481.0

As is well known, solutions of chromium salts become green at a temperature between 70° and 80°. In this latter state they cease to have the power to deposit crystals. Recoura[1] has shown that the green modification is a well defined basic salt mixed with free acid, and Monti[2] has found that the change in color is accompanied by a rise in the conductivity. The recent work of Whitney,[3] using two widely different methods, confirms Recoura in his conclusion that the green modification is a basic salt and that free sulphuric acid is present in the solution. In order to determine whether the passage over into the green modification is discontinuous at any point, a series of experiments was made by placing the conductivity cell, containing a solution of ammonium chrome alum, in a bath, and regularly increasing the temperature with the time. Noting the temperature, the conductivity measurements were made at more or less regular time intervals.

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[1] Ann. chim. phys., [7], 4, 494.

[2] Ztschr. anorg. Chem., **12**, 75.

[3] Ztschr. phys. Chem., **20**, 40.

The following results can be regarded as relatively correct, but on account of the difficulty in measuring the temperature these values are probably each a little too low. In the following table are the conductivity results for a one-twentieth gram-molecular normal solution of ammonium chrome alum, for temperatures from 37°.5 to 90°.

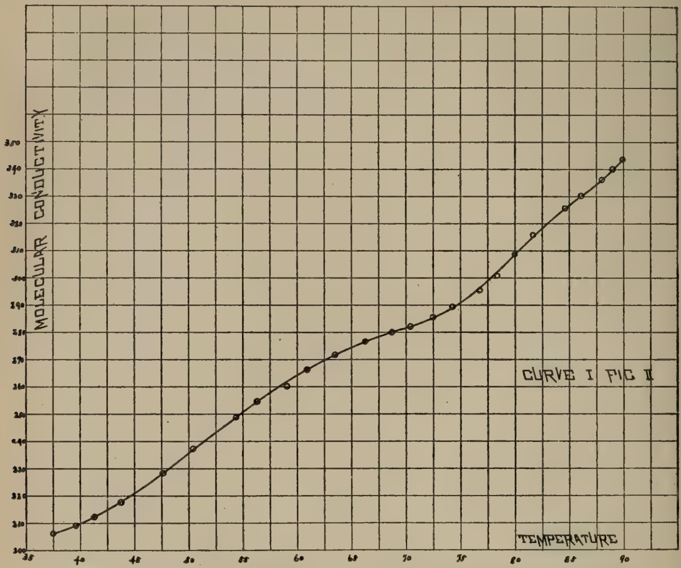
Table XI.

Temperature.	Time. Minutes.	μ_v.
37°.5	..	207.0
39°.5	6	209.8
41°.4	8	213.6
43°.5	10	218.8
47°.5	13	229.2
50°.4	15	236.4
52°.5	17	243.0
54°.5	19	248.4
56°.5	20	254.4
59°.0	22	260.6
61°.0	24	266.0
63°.5	25	271.4
66°.4	28	277.0
68°.4	30	280.2
70°.4	32	283.0
72°.4	33	286.6
74°.3	..	290.0
76°.7	38	295.2
78°.4	40	301.2
80°.2	42	309.4
81°.8	..	316.8
83°.4	45	321.8
84°.7	..	325.8
86°.2	48	330.4
88°.0	..	336.4
89°.2	..	340.6
90°.0	53	343.4

These results are plotted in Curve 1, Fig. II, from which it will be seen that the transformation to the green modification is continuous as the temperature rises.

Ammonium Iron Alum.

A solution of the recrystallized salt was standardized by re-



ducing the ferric to ferrous iron, and reoxidizing the iron by means of standard potassium permanganate. The results of analysis were:

I. 0.24772 gram of $NH_4Fe(SO_4)_2 + 12H_2O$ in 1 cc.
II. 0.24722 " " " " 1 "
Mean 0.24747 " " " " 1 "

The solution was therefore 0.5089 gram-molecular normal. Table XII gives the results of the measurements of the conductivity.

Table XII.

$NH_4Fe(SO_4)_2 + 12H_2O = 482.24.$

Gram-molecules per liter.	Volume.	$\mu_v 25°$.
0.25	4.0	118.9
0.05	20.0	177.4
0.025	40.0	211.5
0.005	200.0	320.2

Instability of Some Alums in Dilute Solution.

In the course of the measurements of the conductivity of dilute solutions of some of the alums, it was observed that the conductivity increased at a more or less rapid rate on standing for a time. As such a change in conductivity must depend upon some change in the condition of the dissolved substance, this observation would indicate that some alums are unstable in the presence of a large volume of water, and, as will be seen, the alums possess different degrees of stability. In table XIII are given the dilutions at which the changes in the conductivity μ_v, with the time which elapsed, were studied.

Table XIII.

Sodium Aluminium Alum.

Volume.	μ_v.	Time.
20000	529.6	0 hours.
"	550.0	24 "

Ammonium Chrome Alum.

Volume.	μ_v.	Time.
20000	630.0	0 hours.
"	686.0	24 "

Ammonium Iron Alum.

Volume.	μ_v.	Time.
200	320.2	0 hours.
"	330.0	2 "
400	411.0	0 "
"	424.0	20 minutes.
2000	694.0	0 "
"	808.8	30 "
"	891.0	18 hours.
"	896.0	21 "

An increase in the conductivity with the time was noticed in the case of the sodium aluminium and ammonium chrome alums, but not until a dilution of approximately 20,000 liters was reached. The former showed an increase of about four per cent. in twenty-four hours. But a much more marked example of instability was brought out in a study of the ammonium iron alum, as is seen in the above table. At a dilution of 200 liters, the conductivity rose three per cent. in two hours. At

400 liters, it showed the same increase in twenty minutes, while at a dilution of 2000 liters, the rate of increase was at first about one and one-half per cent. per minute. This rate quickly diminished with time, and at the end of twenty-four hours an apparent state of equilibrium was reached, with a total increase in the conductivity of about thirty per cent. When the experiment was conducted at 0°, a dilution of 1000 liters was reached before decomposition began. The precipitate formed in the decomposition of the ferric ammonium alum did not appear until after the change in conductivity was observed.

Examples of the rise in the conductivity of dilute solutions have been observed by Kohlrausch[1] in the case of barium nitrate, copper sulphate, and other salts. For the first compound, this was clearly caused by the formation of a basic salt, and the liberation of free acid. The ease with which chromium forms basic salts with rise in temperature has already been considered. The well known tendency of iron ammonium alum to form basic salts is doubtless the cause of the rise in the conductivity of this substance, due to the action of a large volume of water. It seems probable, therefore, that a similar change occurs in very dilute solutions of sodium aluminium and ammonium chrome alums. Such a change would be analogous to that studied by Rose[2] in the case of acid potassium sulphate, which is decomposed by a large volume of water, forming the neutral sulphate and free acid.

Comparison of Conductivity Results.

If the conductivities of the alums are compared, it will be seen that throughout all dilutions, these bear the same relation to one another as the conductivities of their constituents. The conductivities of potassium, sodium and ammonium sulphates stand in the same order as the conductivities of the corresponding alums. A detailed comparison of the conductivities of the alums with the arithmetical mean of the conductivities of their constituents, is given in the tables which follow. The data for the values of the conductivity of aluminium sulphate have been taken from our own results for that compound, supplemented by those of Walden,[1] by interpolation by the graphic method. The data for sodium sulphate are interpolated values from Kohlrausch's[2] tables, reduced to 25° and changed to molecular conductivity units. The values for potassium sulphate and chromium sulphate are taken directly from the tables already given. No data for ammonium sulphate and ferric sulphate are at present available. Since the latter exists only in acid solution, direct observations of its conductivity would have no value for the present purpose.

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[1] Ann. der Phys. Wied., **26**, 175.

[2] Ann. der Phys. Pogg., **82**, 545.

Table XIV.

Potassium Aluminium Alum.

Volume.	K_2SO_4 $\mu_v 25^\circ$.	$Al_2(SO_4)_3$ $\mu_v 25^\circ$.	Arithmetic mean.	Alum observed. $\mu_v 25^\circ$.	Difference, per cent.
5.0012	172.7	108.0	140.3	133.9	—4.5
8.0	183.3	124.2	153.7	149.2	—3.0
20.0	205.1	158.1	181.6	178.3	—1.7
40.0	220.3	185.7	203.0	202.5	—0.2
200.0	252.4	290.4	271.4	269.0	—0.8
400.0	262.2	342.6	302.4	305.2	+0.9

Table XV.

Sodium Aluminium Alum.

Volume.	Na_2SO_4 $\mu_v 25^\circ$.	$Al_2(SO_4)_3$ $\mu_v 25^\circ$.	Arithmetic mean.	Alum observed. $\mu_v 25^\circ$.	Difference. Per cent.
20.0	171.5	158.1	164.8	161.6	—1.9
40.0	183.1	185.7	184.4	184.6	+0.1
200.0	211.6	290.4	251.0	250.6	—0.2
400.0	219.1	342.6	280.8	285.4	+1.6

Table XVI.

Potassium Chrome Alum.

Volume.	K_2SO_4 $\mu\ 25^\circ$.	$Cr_2(SO_4)_3$ $\mu_v 25^\circ$.	Arithmetic mean.	Alum observed. $\mu_v 25^\circ$.	Difference. Per cent.
10.0	187.0	139.0	163.0	147.9	—9.2
20.0	205.1	162.7	183.9	170.4	—7.3
40.0	220.3	190.7	205.5	195.2	—5.0
200.0	252.4	288.2	270.3	266.6	—1.3
400.0	262.2	346.5	304.3	305.5	+0.4
2000.0	276.5	558.2	417.3	418.7	+0.3
4000.0	281.9	671.2	476.5	472.0	—0.9

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[1] Ztschr. phys. Chem., **1**, 541.

[2] Ann. der Phys. Wied., **26**, 196.

A study of the preceding tables seems to justify the following statements: First, in concentrated solutions the conductivity of the alums is notably less than the mean of the conductivities of their constituents; second, the "difference" is very nearly the same for the aluminium alums, while it becomes much greater for the chrome alum; third, the difference grows rapidly less with increasing dilution, so that at 40 liters for alnminium alums, and at about 400 for the chrome alum, it has practically disappeared.

Deductions from these facts must depend upon the relations which exist between the conductivity of a mixture of two electrolytes having a common ion, and the conductivities of the constituents taken separately. It has been shown, especially by the work of Bender and Klein, that in such mixtures the conductivity is in general less than the mean of the conductivities of the constituent salts. But Klein showed that the difference was much greater, when the salts were capable of forming a double salt. Thus, while potassium sulphate and sodium sulphate gave a difference of one per cent., potassium sulphate with ferrous sulphate gave a difference of six per cent. The "difference" found for the more concentrated solutions of the alums, is of the same order of magnitude ($2\frac{1}{2}$ to 11 per cent.), as that found by Klein for the double salts which he studied.

The condition that two electrolytes, having a common ion, may mix without undergoing a change in ionization, has been deduced from the dissociation theory of electrolytic conduction by Arrhenius.[1] If no change in volume occurs on mixing, that condition is that the concentration of the ions, *i. e.*, the quotient of the coefficient of ionization divided by the volume containing one gram-molecule, shall be the same for both solutions, or

$$\frac{\alpha_1 n_1 v_1}{v_1} = \frac{\alpha_2 n_2 v_2}{v_2},$$

where α_1, α_2 are the coefficients of ionization of the respective solutions; n_1, n_2 the number of gram-molecules contained respectively in a unit of volume of each; and v_1, v_2, the respective volumes of the solutions mixed. The following table shows the extent to which this condition is fulfilled in some of the solutions of alums which we employed. On the assumption that we may regard a solution of an alum as having been formed by mixing equal volumes of solutions of its constituents of the same molecular concentration, n_1 and n_2 in the preceding equation become equal, as also v_1 and v_2, and it is necessary only to compare the values of α_1 and α_2 for the constituent solutions.

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[1] Ztschr. phys. Chem., **2**, 284.

The values of α have been calculated from freezing-point data instead of from conductivity, since the experimental error in measuring μ_∞ for aluminium sulphate may become very large. For potassium sulphate, the two methods yield concordant results, as is shown in the table given by Arrhenius.[1] In calculating the values of i, the ratio between the observed and the normal osmotic pressure, the value 1.88 was taken as the normal molecular lowering. The corresponding values of α are calculated from the equation

$$i = 1 + (K - 1)\,\alpha,$$

in which K denotes the number of ions into which each molecule dissociates; *three* for potassium sulphate and *five* for aluminium sulphate.

Table XVII.

Gram-molecules per liter.	K_2SO_4.		$Al_2(SO_4)_3$.		$Cr_2(SO_4)_3$.	
	i.	α.	i.	α.	i.	α.
0.117	2.22	0.61	...	...	2.20	0.30
0.1086	2.28	0.64	2.13	0.28	...	...
0.10	2.30	0.65	...	...	2.21	0.30
0.098	...	...	2.21	0.30	...	...
0.088	2.33	0.66	...	...	2.28	0.32
0.0653	...	...	2.34	0.33	...	...
0.059	2.41	0.70	...	...	2.40	0.35
0.054	2.45	0.72	...	...	...	...
0.05	2.44	0.72	2.44	0.38	2.44	0.38
0.0333	2.57	0.78	...	...	...	...
0.0294	2.57	0.78	...	...	2.55	0.387
0.026	...	...	2.60	0.40	...	...

It is thus apparent that the values of α, and therefore of

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[1] Ztschr. phys. Chem., **2**, 491.

$\frac{\alpha}{v}$, or the concentration of the ions of potassium sulphate, differs widely from that for either aluminium or chromium sulphate, while for the last two the values of α show an almost complete agreement throughout the range of dilutions given. The change in the dissociation produced by mixing either chromium or aluminium sulphate with potassium sulphate, whatever it may be, should therefore be nearly the same in both cases, if we neglect the effect of changes in volume, which in these cases is extremely small. Reference to the preceding tables shows that the difference is by no means the same for the aluminium and chromium alums; the "difference" being four or five times greater in the case of the chromium alum at the same dilution. It is also much greater, if we compare the solution at equal distances from the point of saturation. If we, therefore, even conclude that the potassium aluminium alum were entirely decomposed in concentrated solution, (which is probably not true), we must still admit that the molecules of the double salt in a concentrated solution of chromium alum are only partially broken down. This conclusion with reference to chromium alum agrees with that reached on other grounds by Carey Lea,[1] who, by the use of a reagent for the detection of free sulphuric acid in the presence of sulphates, finds that chrome alum is the only one present as such in solution.

In order to determine whether the solution of an alum is simply equivalent to a mixture of solutions of its constituents, a number of mixtures of equal volumes of solutions of potassium sulphate and aluminium sulphate of the same molecular concentration were prepared, and also of potassium sulphate and chromium sulphate. The conductivities of the constituent salts were observed, then that of the mixture. The results are given in Tables XVIII and XIX.

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[1] Ztschr. anorg. Chem., 4, 445.

Table XVIII.

Potassium Sulphate and Aluminium Sulphate.

Gram-molecules per liter.	K_2SO_4 $\mu_v 25°$.	$Al_2(SO_4)_3$ $\mu_v 25°$.	Mean.	Mixture observed $\mu_v 25°$.	Difference, per cent.
0.2175	170.2	105.7	137.9	129.1	—6.4
0.10855	186.9	130.3	158.6	151.8	—4.3
0.05427	202.8	153.6	178.2	174.2	—2.2
0.03333	213.9	172.5	193.1	190.1	—1.6
0.01666	229.1	202.2	215.6	214.3	—0.6

Table XIX.

Potassium Sulphate and Chromium Sulphate.

Gram-molecules per liter.	K_2SO_4 $\mu_v 25°$.	$Cr_2(SO_4)_3$ $\mu_v 25°$.	Mean.	Mixture observed $\mu_v 25°$.	Difference, per cent.
0.333	157.4	94.2	125.8	113.0	—10.1
0.250	167.9	107.3	137.6	125.1	—9.0
0.100	187.0	139.0	163.0	155.1	—4.9
0.05	205.1	162.7	183.9	177.9	—3.3
0.025	220.3	190.7	205.5	202.8	—1.3

The conductivity of the mixture is thus always less than the mean of the conductivities of the constituent sulphates, the "difference" being greater the more concentrated the solutions. This is the same fact which was observed in the case of the alums, whose conductivity was less than the mean of their constituents.

On comparing the conductivities of the mixtures with those of the alums at the same concentrations, a close agreement is observed in the case of potassium aluminium alum, showing that we may regard a solution of this alum as having been formed by mixing equal volumes of solutions of its constituents of the same molecular concentration. A striking fact is brought out by comparing the conductivity of potassium chrome alum with that of the "mixtures" of the same concentration, the conductivity of the alum being less than that of the mixtures. It must be observed that volume changes play an unimportant part in this connection, since, according to Gerlach[1] the contraction at 15°, for a mixture of potassium and aluminium sulphates containing 0.21 gram-molecule per liter, is 0.06 per cent., and for a mixture of potassium and chromium sulphates, containing 0.27 gram-molecule per liter, is at the same temperature, 0.12 per cent. If the difference noticed is well founded, it might be accounted for by supposing that the molecules of the double salt remain, in part, undecomposed and therefore not completely dissociated into the simplest ions, when its crystals are dissolved, but that the molecules of the constituent salts do not necessarily unite when their solutions are mixed. This is the explanation offered by Graham[1] of the fact observed by him, that the diffusion of the double sulphates of potassium and magnesium differed from that of a mixture of its constituent salts. The conclusions drawn in reference to potassium chrome alum, based on isohydric considerations, cannot perhaps be regarded as absolutely proven from the conductivity measurements alone, but must be regarded as highly probable.

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[1] Ztschr. anal. Chem., **28**, 505.

Summary of Conductivity Results.

The preceding results, in so far as they bear upon the existence of the alums as such in solution, may be summarized as follows:

1. The alums, in dilute solution, have a conductivity which is almost exactly the mean of the conductivities of their constituents, from which it follows that the complex alum molecules are broken down completely in such solutions, into the molecules of the simpler sulphates, and that these simpler molecules dissociate as if alone, barring the effect on the dissociation produced when the solutions are not isohydric.

2. In concentrated solutions the alums show a conductivity less than the mean of the conductivities of their constituents. The difference becomes more marked as the concentration increases and is of the same order as that observed for other double sulphates. It is much greater than that found in the case of mixtures of sulphates incapable of yielding a double salt. This must be regarded as evidence that the alums are partially undecomposed into the constituent molecules in such solutions, or that the dissociation into the simple ions into which the single sulphates break down is not complete.

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[1] Phil. Trans. Lond., 1850, I.

3. The magnitude of the "difference" for potassium chromium alum, as compared with the aluminium alums, affords strong evidence that this alum at least, exists as such in moderately concentrated solutions.

Freezing-Point Measurements.

The apparatus used in the freezing-point determinations was of the ordinary Beckmann form, the inner tube containing the solution being considerably larger than in the ordinary apparatus, to prevent the possibility of touching the bulb of the thermometer with the stirrer. This tube contained no side tube. The solutions used were made up from the same standardized solutions as were employed in the conductivity work. The freezing-point was determined as quickly as possible after the solutions were prepared. In every determination, the zero of the water used in making up that solution, was taken.

The following tables contain the freezing-point lowerings obtained for the alums and their constituent salts.

G denotes the number of grams of the salt in a liter of solution; N the number of gram-molecules per liter. L denotes the corrected lowering of the freezing-point, corrected for the change in concentration of the solution due to the separation of ice, according to the formula deduced by one of us:

$$T = \frac{su}{w}[1]$$

in which T is the fraction of the liquid which solidifies, s the specific heat of the liquid, u the amount of undercooling in degrees Celsius, and w the heat of solidification of a unit weight of the liquid. Δ denotes the gram-molecular lowering of the freezing-point.

In the case of the alums the double formulas are used in expressing the freezing-point lowerings, for convenience in comparison with the lowerings of their constituents, the sum of the lowerings for the constituents being then directly comparable with the lowerings of the alums themselves.

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[1] Jones, Phil. Mag., **36**, 468.

Table XX.

K_2SO_4 = 174.34, 1st Series.

No.	G.	N.	L.	Δ.
1	37.857	0.217	0.890°	4.10
2	18.9285	0.1086	0.466	4.29
3	9.4643	0.0543	0.250	4.61
4	5.8110	0.0333	0.161	4.83
5	2.9055	0.0167	0.084	5.03

Table XXI.

K_2SO_4 = (174.34), 2nd Series.

No.	G.	N.	L.	Δ.
1	58.1134	0.333	1.311°	3.93
2	43.5850	0.250	1.004	4.02
3	17.434	0.100	0.432	4.32
4	8.717	0.050	0.230	4.60
5	4.3585	0.025	0.122	4.88

Table XXII.

$Al_2(SO_4)_3$ = (342.34), 1st Series.

No.	G.	N.	L.	Δ.
1	44.740	0.131	0.516°	3.94
2	33.555	0.098	0.410	4.18
3	22.370	0.0653	0.288	4.41
4	15.659	0.0457	0.212	4.64
5	8.948	0.0261	0.127	4.87
6	6.711	0.0196	0.101	5.15
7	4.474	0.0131	0.073	5.57

Table XXIII.

$Al_2(SO_4)_3$ = 342.34. 2nd Series.

No.	G.	N.	L.	Δ.
1	74.338	0.217	0.832°	3.83
2	37.169	0.1086	0.438	4.03
3	18.5845	0.0543	0.245	4.51
4	11.411	0.0333	0.189	4.77
5	5.7055	0.0166	0.088	5.30

Table XXIV.

$Cr_2(SO_4)_3 = 392.58.$

No.	G.	N.	L.	Δ.
1	130.860	0.333	Salt probably separated on freezing.	
2	98.145	0.250	1.029°	4.12
3	39.258	0.100	0.417	4.17
4	19.629	0.05	0.230	4.60
5	9.8145	0.025	0.121	4.84

Table XXV.

$(NH_4)_2SO_4 = 132.16.$

No.	G.	N.	L.	Δ.
1	26.432	0.2	0.829°	4.145
2	13.216	0.1	0.437	4.370
3	9.2512	0.07	0.316	4.514
4	6.608	0.05	0.237	4.740
5	3.9648	0.03	0.148	4.933
6	1.9824	0.015	0.075	5.00

Table XXVI.

$K_2Al_2(SO_4)_4 + 24H_2O = 948.82.$

No.	G.	N.	L.	Δ.
1	47.441	0.05	0.409°	8.18
2	35.5807	0.0375	0.320	8.53
3	23.720	0.025	0.222	8.88
4	11.8575	0.0125	0.120	9.60
5	4.7430	0.005	0.057	11.40

Table XXVII.

$Na_2Al_2(SO_4)_4 + 24H_2O = 916.66.$

No.	G.	N.	L.	Δ.
1	22.9165	0.025	0.229°	9.16
2	11.4582	0.0125	0.125	10.00
3	5.7291	0.00625	0.009	11.04

Table XXVIII.

$(NH_4)_2Al_2(SO_4)_4 + 24H_2O = 906.6.$

No.	G.	N.	L.	Δ.
1	45.330	0.05	0.408°	8.16
2	33.997	0.0375	0.318	8.48
3	22.665	0.025	0.224	8.96
4	11.332	0.0125	0.121	9.68
5	5.666	0.00625	0.066	10.56

Table XXIX.

$K_2Cr_2(SO_4)_4 + 24H_2O = 999.0.$

No.	G.	N.	L.	Δ.
1	117.44	0.117	0.888°	7.59
2	88.08	0.088	0.686	7.80
3	58.72	0.059	0.480	8.14
4	29.36	0.0294	0.267	9.08
5	17.618	0.0176	0.170	9.66
6	11.744	0.0117	0.119	10.17
7	5.872	0.0059	0.065	11.02

Table XXX.

$(NH_4)_2Cr_2(SO_4)_4 + 24H_2O = 956.8.$

No.	G.	N.	L.	Δ.
1	92.740	0.097	0.768°	7.92
2	46.370	0.0484	0.400	8.26
3	27.822	0.0291	0.266	9.14
4	16.6932	0.0174	0.168	9.65
5	11.1288	0.0116	0.117	10.09
6	5.5644	0.0058	0.064	11.04

Table XXXI.

$(NH_4)_2Fe_2(SO_4)_4 + 24H_2O = 964.42.$

No.	G.	N.	L.	Δ.
1	247.72	0.257	1.820°	7.08
2	185.79	0.192	1.400	7.29
3	123.86	0.128	0.927	7.24
4	92.895	0.096	0.713	7.43
5	61.930	0.064	0.505	7.89
6	37.158	0.0385	0.322	8.36
7	24.772	0.0257	0.227	8.83
8	12.386	0.0128	0.121	9.45
9	6.193	0.0014	0.066	10.31

Comparison of Freezing-Point Results.

Comparing the results for the different alums, as shown in the foregoing tables, it is seen that as regards the aluminium alums, the sodium alum (Table XXVII) gives a somewhat greater depression, for corresponding dilutions, than either the potassium (Table XXVI) or the ammonium (Table XXVIII) alum. The lowerings given by potassium alum correspond closely to, but are slightly greater in concentrated solutions than those of the ammonium alum. In the more dilute solutions the reverse is true, but since the experimental error is here much larger, less value is to be attached to the results. The ammonium chrome and potassium chrome alums show closely agreeing values for corresponding dilutions (Tables XXIX and XXX), while these values are somewhat greater for the same dilutions than those of the aluminium alums.

In the following tables a comparison of the lowerings produced by the alums themselves with the sum of the lowerings of their constituents at the same dilution is given. The values for the constituent salts are interpolated from Tables XX to XXV.

Table XXXII.

Potassium Aluminium Alum.

N.	K_2SO_4 Δ.	$Al_2(SO_4)_3$ Δ.	Sum.	K-Al-alum. Δ.	Difference.
0.05	4.61	4.60	9.21	8.18	1.03
0.0375	4.76	4.72	9.48	8.53	0.95
0.025	4.89	4.91	9.80	8.88	0.92
0.0125	5.02	5.61	10.63	9.60	1.03

Table XXXIII.

Ammonium Aluminium Alum.

N.	$(NH_4)_2SO_4$ Δ.	$Al_2(SO_4)_3$ Δ.	Sum.	Amm-Al.-alum Δ.	Difference.
0.05	4.74	4.55	9.29	8.16	1.13
0.0375	4.86	4.72	9.58	8.48	1.10
0.025	4.95	4.01	9.86	8.96	0.90
0.0125	5.02	5.61	10.63	9.68	0.95

Table XXXIV.

Potassium Chrome Alum.

N.	K_2SO_4 Δ.	$Cr_2(SO_4)_3$ Δ.	Sum.	K-Cr-Alum Δ.	Difference.
0.117	4.28	4.16	8.44	7.59	0.85
0.088	4.38	4.27	8.65	7.80	0.85
0.059	4.54	4.51	9.05	8.14	0.91
0.0294	4.83	4.80	9.63	9.08	0.55

Table XXXV.

Ammonium Chrome Alum.

N.	$(NH_4)_2SO_4$ Δ.	$Cr_2(SO_4)_3$ Δ.	Amm-Cr-alum. Sum.	Observed.	Difference.
0.097	4.38	4.19	8.57	7.92	0.65
0.0484	4.76	4.61	9.37	8.26	1.11
0.0291	4.93	4.81	9.74	9.14	0.60

The results here tabulated show that the lowerings produced by the alums, in the more concentrated solutions, are uniformly 10 to 11 per cent. less than the sum of the lowerings of their constituents, ammonium chrome alum excepted. Here the difference is considerably smaller, being only about 7.3 per cent. This is probably due to some experimental error, since other values obtained for this compound are in agreement with those for the other alums.

Raoult[1] found a lowering for potassium aluminium alum, which was only 1.2 of a per cent. less than the sum of the lowerings of the constituents. He inferred that the decomposition of the alum molecules in solution was complete. He does not, however, state the concentration which he employed and that is of course of importance in this connection.

The freezing-point determinations which we have carried out must be regarded as confirming the evidence from conductivity, that the alum molecules exist to some extent in the more concentrated solutions.

SILICIDES OF COPPER AND IRON.

By G. de Chalmot.

Copper Silicide.—In a former article[2] I described a crystalline silicide of copper having probably the composition Cu_2Si_3. At the time I had not much more of this material than was necessary for analysis, and lack of time prevented me from carrying the investigation further. At about the same time Vigoureux[3] published an article in which he described the compound Cu_2Si, and wherein he makes it appear unlikely that any other copper silicide containing more silicon than Cu_2Si exists.

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[1] Compt. rend., **99**, 914.

[2] This Journal, **18**, 95.

[3] Compt. Rend., **122**, 318.

I have now investigated this matter again, and I have found that the crystals which I described are in fact no chemical compound, but a mixture of silicon, copper silicide, and copper.

I found at the time that *aqua regia* decomposes only a part of the crystals, but examining the undissolved residue, I found it to contain copper. I have now, however, succeeded in extracting all the copper from this residue, in case the material was very finely pulverized and heated for a considerable time with the acid mixture, and I have shown that the residue contained crystalline silicon. There is another reason why I did not give due attention to the fact that *aqua regia* attacks only a part of the crystals. I found that it does not completely decompose copper-silicon alloys containing only 13 to 14 per cent. of silicon. In regard to this subject I shall have more to say presently.

It is a remarkable coincidence, that in several instances I have found the composition of these crystals to be about that represented by the formula Cu_2Si_3. In other cases, however, they contain much more silicon, and especially when they appear to be purer. This led me to the belief that absolutely pure crystals would prove to consist only of silicon, but a small sample which was very carefully selected, with the aid of a strong glass, contained only 55.67 per cent. of silicon. I also picked out under the microscope several small apparently quite pure crystals, and treated them with cold *aqua regia*. They invariably broke up into many small pieces, and a considerable amount of copper was dissolved. Several of the small silicon crystals, which result from this treatment, retain the same brilliancy as the crystals of which they formed a part. The most perfect crystals are found in cavities in the interior of the pieces of copper silicide, that are formed in the furnace. These crystals are very flat, and of great brilliancy. They have very sharp edges and corners.

Vigoureux called attention to the fact that the copper-silicon alloys tarnish easily and become reddish. The crystals in question also tarnish, but only in spots or lines, most places remaining brilliant bluish-white. They sometimes assume an appearance as if they were cracked all over. The outer surface, therefore, may mainly be formed by silicon crystals. I have found similar crystalline formations in alloys of manganese and iron with silicon. In the case of manganese I have shown them to contain crystalline silicon, and the compound $MnSi_2$.

In order to find out whether the copper in the crystals was present in the form of the compound Cu_2Si, or as a silicide containing more silicon, I determined the composition of several samples and also the amount of free silicon which they contained. For determining the latter, I pulverized the material and sifted it through fine linen. I then heated it for 6 to 8 hours with *aqua regia* and, after diluting with water, I filtered off the mixture of silica and silicon. I dried the filter, scraped from it its contents, and, after burning it, I added filter contents and filter ashes together, and treated them for 24 hours with strong hydrofluoric acid, in order to dissolve the silica and the iron silicide. The remaining silicon was fused with soda and saltpeter, and the silicon and iron were determined by the usual methods. I say iron was determined, because small amounts, mostly very small and not over 0.15 per cent., often withstand the action of the hydrofluoric acid. This iron was supposed to be present as the compound $FeSi_2$, and a corresponding amount of silicon was deducted from the insoluble silicon that was found. By this method the results are more accurate than by simply weighing the insoluble silicon, for in the latter case the presence of any graphite or other matter insoluble in hydrofluoric acid impairs the value of the result. I obtained the following results:

	I.	II.	III.
Total silicon	55.67	39.14	41.53
Copper	43.83	60.32	57.40
Iron	0.50	0.67	0.42
Calcium	....	....	1.08
Insoluble silicon	47.00	28.61[1]	27.50

Sample I was very pure and was picked out with great care with the help of a strong glass. Samples II and III contained more or less of the surrounding micro-crystalline mass in which the crystals are imbedded.

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[1] Average of two analyses, the results of which agree well with each other.

The copper determination of No. 1 was lost, for which reason the percentage of copper was found by deduction. Assuming that iron and calcium are present in the form of $CaSi_2$ and FeSi,[1] I calculate the relative amounts of copper and of silicon combined with it as follows:

	Found.			Calculated for
	I.	II.	III.	Cu_2Si.
Cu	84.29	85.95	82.61	81.71
Si	15.71	14.05	17.39	18.29

It appears from these analyses that where a large excess of silicon is present, as in these crystals, no silicides are formed that contain more silicon than the compound Cu_2Si. There is even less silicon united with the copper than would be the case if the latter were present only in the form of Cu_2Si. It is possible either that a part of the copper is present as a silicide containing less silicon, or a part of the copper may be in the free condition. In order to find this out I examined Sample No. II, which apparently contains the largest excess of copper. I rubbed a part of the finely pulverized material with mercury in a mortar. The mercury was then pressed through four layers of linen until it proved to be free from adherent particles of crystals when examined with a glass. The mercury was now evaporated from a porcelain crucible. It left a considerable deposit of cuprous oxide, which dissolved with a green color in strong hydrochloric acid, and was further detected by the usual reagents, *i. e.*, ammonia and potassium ferrocyanide. It had been previously ascertained that the mercury which was used left no residue on evaporation.

It is not at all probable that mercury dissolves copper unless the latter is in the free condition. The mercury, moreover, did not dissolve silicon and, that it should decompose a silicide, if simply rubbed with it in a mortar, seems still more improbable. In the same manner I showed the presence of considerable amounts of free copper in an alloy containing 26 per cent. of silicon, the copper of which had been six hours in the furnace.

The result of this mercury test confirms the results of the analyses. We have here an interesting case where free copper, free silicon, and copper silicide exist side by side in the electric furnace. The copper had certainly time enough to combine with silicon, for in all cases it had been in the electric furnace for at least two hours. It might also be suggested that all the copper had not been in or very near to the arc, and that it unites with silicon only at such a place, but silicon and copper unite at a much lower temperature, for example in a blast furnace.

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[1] See this JOURNAL, 18, 539,

We seem to have here a case of chemical equilibrium between copper silicide, Cu_2Si, and its dissociation products, copper and silicon, which can be compared with the dissociation of carbonic acid into the monoxide and oxygen. So far as I know this is the first case of the kind observed in the preparation of carbides, silicides or other similar compounds in the electric furnace. From these results it seemed to me likely that free silicon should occur in silicon alloys containing less silicon than the compound Cu_2Si.

Vigoureux says that copper silicon alloys up to nearly 20 per cent. of silicon are quite homogeneous, and do not contain free silicon. I had previously found that *aqua regia* does not completely decompose alloys containing 13–14 per cent. of silicon. By further examination I found for example that a sample of alloy made in the electric furnace contained:

Total silicon	14.22
Free crystalline silicon	1.65

This agrees with my former deductions. I cannot say how far the difference in the method of preparation of the alloys has affected the results.

Vigoureux worked with mixtures of silicon and copper for a few minutes, and I heated a mixture of silica and carbon for several hours in a furnace with a copper cathode.

Iron Silicides.—Iron silicides of the following formulas have been described: Fe_2Si,[1] Fe_3Si_2,[2] $FeSi$[3] and $FeSi_2$.[4] Hahn obtained the latter compound by treating the impure silicide, Fe_2Si, with hydrofluoric acid, and he describes it as an insoluble residue. Moissan was unable to obtain a similar re-

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[1] Hahn: Ann. Chem. (Liebig), **129**, 57; Moissan: Compt. rend., **121**, 621.

[2] J. Am. Chem. Soc., **17**, 923.

[3] Hahn: loc. cit.

[4] Hahn: loc. cit.

OF THE
UNIVERSITY of ILLINOIS.

sult, which makes Hahn's statement appear doubtful. I had several reasons to believe in the existence of a compound $FeSi_2$, but I believed it to be soluble in hydrofluoric acid. I can easily obtain iron-silicon alloys containing 35-40 per cent. of silicon, which are entirely soluble in hydrofluoric acid, and therefore do not contain free silicon. I also obtained in the electric furnace an alloy containing 46.22 per cent. of silicon, which apparently did not contain free silicon, but I did not test at the time whether this alloy was soluble in hydrofluoric acid.

I now took an alloy of about 39 per cent. of silicon, pulverized it well, and, after having mixed it with water, I added a little hydrofluoric acid at a time, adding from time to time more water, and cooling the platinum dish all the time. After the most violent reaction was over, I allowed the dish to stand for 24 hours. I found in it a residue of gray, metallic crystals, which contained:

I.	II.	Calculated for $FeSi_2$.
48.26	49.71	50.16
52.24	50.56	49.84

The yield was small—about 20 per cent. The compound, $FeSi_2$, therefore, undoubtedly exists, and it finds its place beside the compounds, $MnSi_2$, $CrSi_2$ and $CaSi_2$. It is completely soluble in cold hydrofluoric acid, especially if the latter is concentrated, but it is less so than the iron silicides, which contain less silicon.

Willson Aluminum Co., Spray, N. C.
November, 1896.

Contributions from the Laboratories of the Massachusetts Institute of Technology.

XV.—FORMATION OF DIACETYLENYL (BUTADIINE) FROM COPPER ACETYLENE.

By A. A. Noyes and C. W. Tucker.

In 1862 Reboul[1] found in passing acetylene into bromine that, in addition to the liquid bromides, there is often formed 6 to 8 per cent. of a crystalline substance. He did not further investigate it, but seems to have thought that it originated from impurities in his acetylene, which, however, was prepared from copper acetylene and hydrochloric acid.

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[1] Compt. rend., **54**, 1229.

In 1875, and again in 1889, Sabanejeff[1] published accounts of quite extended investigations on the formation and properties of this bromide. The largest yield (6 per cent.) was obtained by passing acetylene (from copper acetylene) into boiling bromine. His analysis showed it to have the empirical formula C_2HBr_3, but a freezing-point determination of its solution in benzene showed that its molecular weight (500 and 504) was about twice that corresponding to this simple formula (265), and he therefore concluded that its symbol is $C_4H_2Br_6$. Molecular silver removed from the compound one-third of its bromine. As the bromide does not take up the full amount of bromine corresponding to bodies of the paraffin series, he believed it to be a ring compound, hexabromtetramethylene, and supposed it to be formed by the polymerization of bromacetylene, and subsequent addition of bromine.

The purpose of our investigation was to establish the constitution of this bromide, and to explain its origin. We first attempted to prepare some of it by passing acetylene generated from calcium carbide into boiling bromine until saturated, as Sabanejeff directs. Five experiments were made, each with a half pound or pound of bromine, the conditions being varied somewhat. In one experiment the bromine was covered with water; in another the acetylene was caused to combine with the bromine vapors above the liquid. But in no case could the slightest separation of crystals be observed, even on cooling the liquid product in a freezing-mixture, or after fractional distillation of it with steam. Acetylene from calcium carbide was then passed into ammoniacal cuprous chloride, the copper compound decomposed by hot hydrochloric acid, and the evolved gas passed into boiling bromine until it was decolorized. On cooling, a considerable quantity of crystals separated, constituting 4 per cent. of the total product. Their properties showed them to be identical with the bromide of Sabanejeff.

It is evident, from these experiments, that the crystals are not produced from pure acetylene, but from some other substance present in the gas resulting from the decomposition of copper acetylene by hydrochloric acid.

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[1] Ann. Chem. (Liebig), **178**, 114; J. Russian Chem. Soc., **21**, 1; Ber. d. chem. Ges., **22 c**, 249.

We next directed our attention to a study of the conditions which determine the yield of the solid bromide ; for the quantity of it obtained varied greatly in different experiments, carried out apparently in exactly the same manner. For example, in five preparations, all made in the manner above described, the amounts of the solid bromide obtained were 2.1, 3.0, 4.0, 1.8, and 1.8 per cent. of the total product, which consisted of 387, 209, 125, 553, and 454 grams, respectively.

It was first determined that the crystalline bromide is formed in just as good yield (4 per cent.) when the copper acetylene is decomposed by potassium cyanide solution instead of hydrochloric acid. It seemed probable from this experiment that the bromide does not owe its origin primarily to the reaction of either of these reagents on copper acetylene, but to some other cause. No further light was thrown on the matter by a study of the effect of varying the conditions of the combination of the gas with the bromine. Better yields, consisting sometimes of 5 per cent., seemed to be obtained when smaller quantities of bromine were used.

The true explanation of the origin of the solid bromide finally became evident when it was discovered that the formation is entirely prevented by the addition of strips of metallic copper to the copper acetylene during its decomposition by the hydrochloric acid. The hydrocarbon corresponding to the bromide is therefore evidently produced by the oxidizing action of cupric chloride formed by contact of its decomposing mixture with the air. If this explanation is correct, the yield should be greatly increased by the direct addition of cupric chloride to the copper acetylene before its decomposition. And it was in fact found that such is the case, 9 per cent. of the crystals being obtained when an equal weight of crystallized cupric chloride was mixed with the copper acetylene. The following experiment was also tried : A measured volume of acetylene was passed into ammoniacal cuprous chloride solution until the latter was saturated ; the precipitate was washed, water and an equal molecular quantity of cupric chloride added to it, and the mixture ($C_2Cu_2+CuCl_2+xH_2O$) heated for three hours on a water-bath. At the end of that time the solution was decolorized, and the cupric chloride completely reduced.

The origin of the hydrocarbon being thus determined, it remained to establish its constitution. It seemed desirable first to confirm the composition and molecular weight assigned to the bromide by Sabanejeff. Analyses of a portion crystallized from boiling benzene, were made with the following results :

I. 0.4875 gram substance gave 0.1661 gram CO_2 and 0.0253 gram H_2O.

II. 0.5715 gram substance gave 0.1917 gram CO_2 and 0.0264 gram H_2O.

III. 0.5587 gram substance gave 1.180 gram AgBr.

	Found.			Calculated for	
	I.	II.	III.	$C_4H_2Br_6$.	$C_4H_4Br_6$.
C	9.29	9.15	9.26	9.07	9.04
H	0.58	0.52	0.53	0.38	0.76
Br	89.76	....	90.31	90.55	90.20

Column III contains Sabanejeff's results, which are seen to agree closely with our own. The percentage composition corresponds to that required by the formula $C_4H_2Br_6$. The formula $C_4H_4Br_6$ is out of the question, for it corresponds to over 0.2 per cent. more hydrogen than that actually found.

The confirmation of the molecular weight is even more important; for in the determination published by Sabanejeff the greatest observed lowering of the freezing-point was only 0°.08. The following determinations were made by Beckmann's boiling-point method, using as a solvent chloroform, whose molecular raising is 36°.6 according to Beckmann's[1] calculation.

Weight of chloroform taken, 40.68 grams.

Weight substance taken.	Weight substance in 100 grams solvent.	Rise in boiling-point.	Molecular weight found.	Calculated for $C_4H_2Br_6$.
0.639	1.570	0.108	532	530
1.335	3.282	0.227	529	....
1.806	4.439	0.292	556	....

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[1] Ztschr. phys. Chem., 6, 445.

There is therefore no doubt that the molecular formula of the substance is $C_4H_2Br_6$, as stated by Sabanejeff.

Incidentally, at this point, the properties of our bromide may be noted. It melted at 183°.5 (corr.) (according to Sabanejeff at 172°–174°). It crystallized in colorless transparent plates belonging to the orthorhombic system. Crystallographic measurements, made for us by Prof. G. E. Barton, showed that the exterior angles were 264° 30′, 303° 30′, and 48° 45′, the prism angle 120° 40′, and that between the brachypinacoid and prism face 57° 15′. When the substance is heated above its melting-point, bromine vapors are evolved; and at 220° under a pressure of 40 mm. a liquid distils over, which recombines partially with the bromine vapors to form the original solid bromide.

We will next consider the constitution of this bromide and the nature of the hydrocarbon from which it is derived. Owing to the fact that, although produced in the presence of a large excess of boiling bromine, it takes up two atoms less than corresponds to saturation,[1] Sabanejeff concluded that it was hexabromtetramethylene, a compound with a closed ring. Since our experiments prove that it is not produced at all when pure acetylene is passed into bromine, his explanation of its formation by the polymerization of bromacetylene is obviously incorrect. It is, however, possible that hexabromtetramethylene might be formed from the closed-ring hydrocarbon $(CH)_4$, a polymer of acetylene, by the substitution of two atoms and the addition of four atoms of bromine. There are, however, two facts which conclusively prove that the bromide does not owe its origin to this hydrocarbon. One is that the hydrocarbon forming the bromide is an *oxidation-product* of acetylene or its copper compounds, as shown by the copper and cupric chloride experiments above described. The other is that the gas evolved from the copper acetylene was several times examined, and in every case found to be completely absorbed by ammoniacal cuprous chloride, thus showing it to consist only of triple-bonded compounds.

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[1] We found, moreover, that even when heated to 140° in a closed tube with a large excess of bromine, the bromide remained entirely unaffected, as was shown by the unchanged melting-point.

The only explanation consistent with these facts is, therefore, that the bromide is formed by the direct union with bromine of the hydrocarbon, C_4H_2, diacetylenyl, or butadiine, and that the latter is formed from copper acetylene by the following reactions:

$$2C_2Cu_2 + 2CuCl_2 = C_4Cu_2 + 2Cu_2Cl_2.$$
$$C_4Cu_2 + 2HCl = CH \vdots C.C \vdots CH + Cu_2Cl_2.$$

It has been shown by Griner[1] that an entirely similar reaction takes place when copper allylene is treated with potassium ferricyanide.

That the hydrocarbon combines only with six atoms of bromine, and not with eight, is to be explained by the principle that halogen compounds which contain as large a proportion of halogen as the hexabromide, even though theoretically unsaturated, have very little tendency to combine with more halogen. In exemplification of this principle, reference may be made to the fact that tetrabromethylene, C_2Br_4, is met with as a product of energetic brominations.[2]

Diacetylenyl has been already obtained by Baeyer[3] from diacetylenedicarbonic acid, but not in sufficient quantity for analysis or determination of its properties. We therefore attempted to separate it from the gas prepared from copper acetylene by passing it through a worm, surrounded by a freezing-mixture. In this way a few cubic centimeters of a liquid were condensed, which boiled from 40°–50° and gave, with bromine, crystals of diacetylenyl hexabromide. But the condensed product contained also a large proportion of a chlorine compound, from which the hydrocarbon could not be separated by distillation.

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[1] Beilstein's Handbuch, **1**, 140.

[2] See Beilstein's Handbuch der organischen Chemie; also, Ber. d. chem. Ges., **11**, 2238.

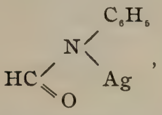
[3] Ber. d. chem. Ges., **18**, 2272.

Contribution from the Sheffield Laboratory of Yale University.

XLVIII.—ON THE ACTION OF ACID CHLORIDES ON THE IMIDO ESTERS AND ISOANILIDES, AND ON THE STRUCTURE OF THE SILVER SALTS OF THE ANILIDES.

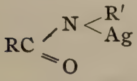
By H. L. Wheeler and P. T. Walden.

It has been shown in recent papers[1] from this laboratory that the silver salts of the anilides react with acid chlorides, giving diacid anilides, and, therefore, as if they had the structure

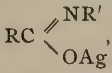


provided the action be considered as a direct replacement or double decomposition. The conclusion that follows from these reactions, with the above proviso, *i. e.*, that the silver salts have the metal joined to nitrogen, is directly opposite to that obtained by the action of alkyl halides.[2] In the latter case it was concluded that the metal was joined to oxygen, since isoanilides or substituted imido ethers were obtained.

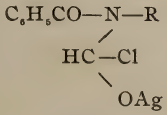
These contradictory reactions are certainly not to be dismissed with the statement that they are due to tautomerism. The products obtained by acting on the silver salts with acid chlorides retained silver halide persistently, and it was considered possible that *the reaction was not a double decomposition, but that it took place first by addition then separation of silver halide.* Two forms of addition-products were considered, according to whether the silver salts are derivatives of the type



or

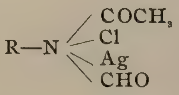


, as follows :



A.

and



B.

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[1] Wheeler and Boltwood : This Journal, 18, 381 ; *Ibid.*, 696.

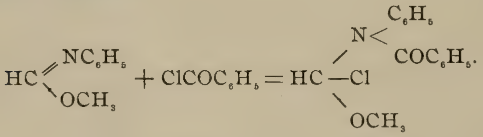
[2] Comstock and Kleeberg : This Journal, 12, 495.

Before proceeding to the discussion of the probable structure of the silver salts, it is evidently desirable to study the action of acid chlorides on compounds that are definitely constituted according to one of the above types. The isoanilides and the free imido esters were therefore selected with the object of determining in what manner the acid chlorides would react with compounds which undoubtedly contain the atomic grouping $RC\begin{smallmatrix}\diagup\!\!\!\!\diagup NR' \\ \diagdown OR''\end{smallmatrix}$ since this grouping is generally assumed to exist in the silver salts of the amides and anilides.

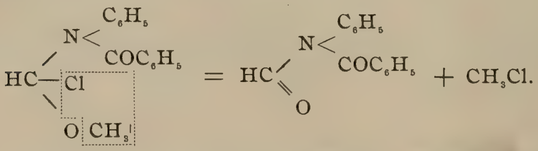
We find that the reaction takes place readily at ordinary temperatures and goes quantitatively in two ways, according to whether the imido group in the imido ester is substituted or not.

The Action of Acid Chlorides on the Isoanilides.

The substituted imido esters or isoanilides react with acid chlorides as follows:

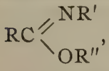


This intermediate addition-product immediately decomposes with the evolution of methyl chloride and a mixed diacid anilide results:



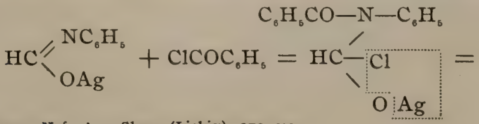
The mixed diacid anilides thus obtained decompose with alkali, giving the mono acid anilide of the higher acid group, thus showing that they have both acid groups attached to nitrogen. That the isoanilides react so readily with acid chlorides is due to the double union between carbon and nitrogen, since, were it otherwise, the acid chloride would have to act by double decomposition on the group $\overset{\|}{—C—}OCH_3$. Such a direct double decomposition is evidently impossible, since it has been found that one of the characteristic properties of the group $\overset{\|}{—C—}OCH_3$ is that it is *not* acted on by acid chlorides. Indeed on this fact is based the general method of determining the presence or absence of this group in compounds which may contain either this or hydroxyl. In such cases, as is well known, the latter alone reacts with acid chlorides. That this reaction is not a direct double decomposition or replacement of the alkyl group by the acid radical is also shown by the fact that non-substituted imido esters react with acid chlorides with the separation of hydrogen chloride instead of alkyl chloride (see below). It is at once evident that the only reaction which will explain the different behavior of the imido esters and isoanilides toward acid chlorides, and which will be general for both cases is that of addition.

The reactions of acid chlorides on the isoanilides and imido esters are the first that have been obtained, in the case of substances that have, or are supposed to have, the structure



$RC\begin{matrix} /\!/ NR' \\ \backslash OR'' \end{matrix}$, which admit of only one general interpretation, and in which the so-called tautomerism or wandering of groups is excluded. They show that the so-called tautomeric or contradictory reactions in the case of the silver salts are to be explained by addition.[1] We are now in a position to discuss the structure of the silver salts.

It is to be noticed that the above reactions of the isoanilides are perfectly analogous to the action of the acid chlorides on the silver salts of the anilides, and the course of the reaction in the latter case is, therefore, to be interpreted as follows, the addition taking place according to type A as given above:



$$HC\begin{matrix} /\!/ NC_6H_5 \\ \backslash OAg \end{matrix} + ClCOC_6H_5 = HC\begin{matrix} / C_6H_5CO—N—C_6H_5 \\ — Cl \\ \backslash O\ Ag \end{matrix} =$$

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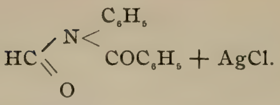
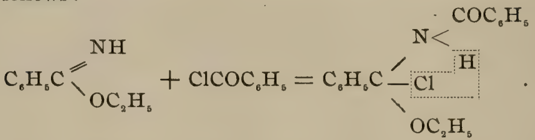
[1] Compare Nef: Ann. Chem. (Liebig), **270**, 293.



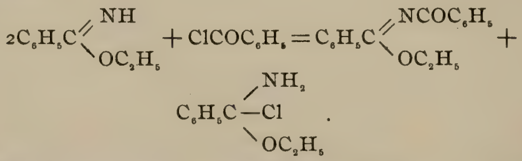
From which it follows that the silver salts of the anilides have the metal joined to oxygen as first stated by Comstock and Kleeberg.[1]

The Action of the Acid Chlorides on the Imido Esters.

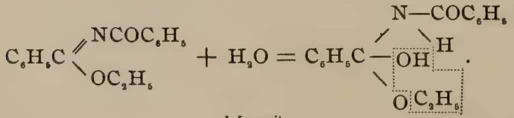
The non-substituted imido esters react with acid chlorides as follows:



This intermediate addition-product, like the preceding, immediately decomposes, not however with the evolution of ethyl chloride, as in the case of the isoanilides, but by separation of hydrogen chloride. (Since chlorine has a greater tendency to unite with hydrogen than with methyl or alkyl.) The hydrogen chloride liberated in this manner combines with the excess of imido ether, and the products obtained are formed as follows:



When the acyl imido esters are treated with acid, or when they are exposed to the air for some time, they take up a molecule of water and decompose into diacid amides as follows:



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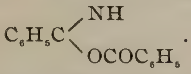
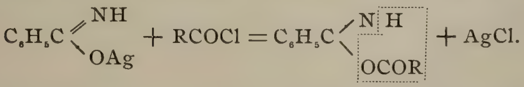
[1] *Loc. cit.*

The above decomposition is perfectly analogous to the action of the silver salts of the amides[1] and anilides[2] with acids, and finally this decomposition proves that the diacid amides—like the diacid anilides—have both acid groups attached to nitrogen, and the statement no longer holds true that diacid amides of the type R—CONHR′ are still unknown,[3] or that in the present state of our knowledge dibenzamide may have the structure[4]



$$C_6H_5C\begin{cases}NH \\ OCOC_6H_5\end{cases}.$$

In fact diacid amides of the latter type, with the acyl group attached to oxygen are probably incapable of existence. This conclusion has been reached through the following considerations: It has been shown in a recent paper[5] from this laboratory that silver benzamide reacts with acid chlorides, giving benzonitrile, and therefore differently from the silver salts of the anilides, which give diacid anilides.[6] It has been shown above that in all probability the action of acid chlorides on silver formanilide takes place by addition. Therefore, in the case of benzamide, it must be double decomposition. (This was previously stated as the only simple explanation.) The resulting isodiacid amide is formed and breaks up as follows:



$$C_6H_5C\begin{cases}NH \\ OAg\end{cases} + RCOCl = C_6H_5C\begin{cases}N\,\boxed{H} \\ \boxed{OCOR}\end{cases} + AgCl.$$

The Action of the Halogens on the Imido Esters. Halogen Imido Esters.

So far only the action of bromine and iodine have been tried. The result is precisely similar to that of the action of acid chlorides, two molecules of the imido ester react with one molecule of halogen, giving halogen imido esters and halogen hydride salts of imido ester, most likely as follows:

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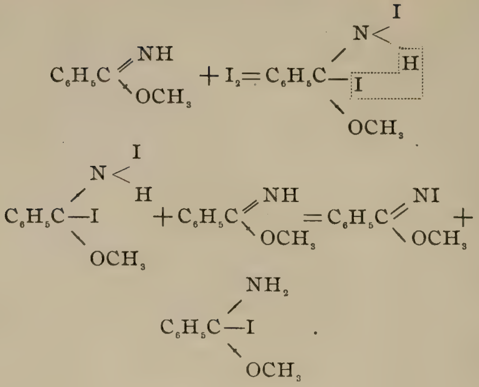
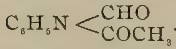
[1] Tafel and Enoch: Ber. d. chem. Ges., **23**, 105.
[2] Comstock and Clapp: This JOURNAL, **13**, 525.
[3] Pinner: *Die Imidoäther und ihre Derivate*, p. 9.
[4] Pinner: Ber. d. chem. Ges., **25**, 1436.
[5] Wheeler: This JOURNAL, **18**, 701.
[6] Wheeler and Boltwood: *Loc. cit.*



EXPERIMENTAL PART.



Formylacetanilide, $C_6H_5N<\begin{smallmatrix}CHO\\COCH_3\end{smallmatrix}$.—Acetyl chloride reacts on phenylformimidoethyl ester[1] at ordinary temperatures with a violent evolution of ethyl chloride. It is best to modify the reaction by diluting with a dry solvent. The following procedure proved satisfactory: Five grams of imido ester were mixed with 5.6 grams of acetyl chloride in a mixture of ether and ligroïn. The evolution of ethyl chloride took place smoothly and a colorless oil separated. The whole was allowed to stand for 12 hours. The oil was then taken up with ether and shaken with a solution of sodium bicarbonate. On evaporating off the ether an oil was obtained which, after standing several days, was distilled at 23 mm. pressure, when practically the entire quantity distilled from 157° to 158°. It was then cooled in a freezing-mixture and, on stirring, it solidified. After pressing on a porous plate, it was crystallized from a mixture of ether and ligroïn, when beautiful, thick, brittle crystals were obtained melting from 56° to 57°. This material proved to be identical with formylacetanilide obtained from silver formanilide and acetyl chloride.[2] On treating it with sodium hydrate, acetanilide was formed.

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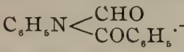
[1] Prepared from the silver salt of formanilide and ethyl iodide: Comstock and Kleeberg, This JOURNAL, *loc. cit.*

[2] This JOURNAL, 18, 698.



Formylbenzanilide, $C_6H_5N\Big<\begin{matrix}CHO\\COC_6H_5\end{matrix}$.—On mixing molecular proportions of phenylformimidoethyl ester and benzoyl chloride, the reaction takes place more quietly than in the previous case. After the evolution of ethyl chloride ceases the material gives needles. When crystallized from alcohol these melt at 112°, and in other respects are identical with the products obtained from silver and mercury formanilide with benzoyl chloride. When treated with sodium hydrate it gives benzanilide. It was stated in a previous paper[1] that "a mixture of benzanilide and formylbenzanilide can readily be distinguished when crystallized from alcohol. The former separates first in needles; the latter forms a supersaturated solution, and on shaking deposits plates." This is a mistake, as it is just the reverse. The formylbenzanilide is the least soluble and comes down first in needles.

Formylbenzenesulphonanilide, $C_6H_5N\Big<\begin{matrix}CHO\\SO_2C_6H_5\end{matrix}$.—Phenylformimidoethyl ester and benzene sulphochloride react slowly at ordinary temperatures. Four grams of the imido ether and 4.7 grams of benzene sulphochloride were mixed and kept at a temperature of about 38° to 43° for two days. The mixture then became semi-solid. It was washed with alcohol and the residue crystallized from strong alcohol, when beautiful, colorless, radiating needles were obtained. These melted at 148°–149°. This material on analysis gave the following results:

	Found.	Calculated for $C_{13}H_{11}NO_3S$.
N	5.2	5.3

Half a gram of the analyzed material was boiled with a 10 per cent. solution of sodium hydrate. Solution took place, and on cooling, nothing separated; dilute hydrochloric acid was then added, and the resulting colorless precipitate was washed with water and dried in the air. It melted at 110° without further purification. This was therefore benzenesulphonanilide. In the case of this mixed diacid anilide, as well as in all previous cases, alkali first removes the lower acid group.

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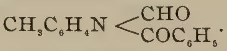
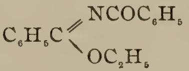
[1] Wheeler and Boltwood: This JOURNAL, 18, 381.

Formylbenzorthotoluide, $CH_3C_6H_4N<\begin{matrix}CHO\\COC_6H_5\end{matrix}$.—Molecular proportions of orthotolylformimidomethyl ester and benzoyl chloride were mixed, and the whole heated to 80° until the evolution of methyl chloride had stopped. The mass was then poured into a little alcohol, when rectangular, colorless, shining plates separated. These melted at 91°, and when carefully crystallized from strong alcohol the melting-point did not change. The melting-point of this compound is therefore 91° and not 92°, as previously stated.[1] It gave benzorthotoluide when treated with alkali.

Formylbenzparatoluide,  $CH_3C_6H_4N<\begin{matrix}CHO\\COC_6H_5\end{matrix}$.—This was prepared from paratolylformimidomethyl ester in the same manner as the preceding compound. It was identical with the compound prepared from mercury formparatoluide and benzoyl chloride.[2] Its melting-point is more nearly 102° than 101°, as previously stated. When treated with alkali it gave benzparatoluide. A similar decomposition into the monoacid anilide is slowly caused when this and the preceding compound are boiled with dilute alcohol.

Acyl Imido Esters.

Benzoylimidoethyl Benzoate,  $C_6H_5C\begin{matrix}\nearrow NCOC_6H_5\\ \searrow OC_2H_5\end{matrix}$. — When benzimidoethyl ester and benzoyl chloride[3] are mixed (in ethereal solution) in the proportion of two molecules of the former to one of the latter, and allowed to stand for 12 hours, snow-white needles separate. These consist of the hydrochloride of benzimidoethyl ester. On filtering and concentrating the ethereal solution, colorless, spear-like or lozenge-shaped crystals separate. These were carefully crystallized from dilute alcohol for analysis. The pure material thus obtained melted at 65°.

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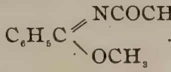
[1] Wheeler and Boltwood: This JOURNAL, 18, 381.

[2] Wheeler and McFarland: This JOURNAL, 18, 540.

[3] The pure benzimidoethyl and methyl esters for this work were prepared according to Bushong's excellent method. This JOURNAL, 18, 490.

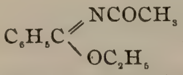
	Found.	Calculated for $C_{16}H_{15}NO_2$.
C	76.3	75.9
H	6.1	5.9
N	5.5	5.5

Benzoylimidoethyl benzoate is stable towards alkali in the cold; acids on the other hand readily convert it into dibenzmide. When the dilute alcoholic solution is warmed with a few drops of dilute sulphuric acid, needles of the diacid amide are obtained, melting at 148°.

Acetylimidomethyl Benzoate,  $C_6H_5C{\diagup\!\!\!\!\diagup\, NCOCH_3 \atop \diagdown\, OCH_3}$.—Benzimidomethyl ester and acetyl chloride, in the proportion of two molecules of the former to one of the latter, were mixed in ethereal solution. After 12 hours the hydrochloride of the imido ester was filtered off, and on evaporating the ether an oil was obtained. This was distilled at 20 mm. pressure, when about one-third passed over below 140°, and the remainder at about this temperature. The portion boiling at 140° was redistilled at 15 mm. A few drops were removed below 139°, and then the remainder boiled almost entirely at this temperature. This fraction on cooling in a freezing-mixture did not solidify. It was analyzed with the following result:

	Found.	Calculated for $C_{10}H_{11}NO_2$.
N	8.12	7.91

The portion mentioned above, boiling below 140°, consisted of unaltered imido ester and benzonitrile (?). When acetylimidomethyl benzoate is mixed with a little alcohol and a few drops of dilute sulphuric acid added, evolution of heat occurs and the whole on cooling solidifies to a mass of colorless prisms or needles. This material is acetylbenzamide, which melts at 120°.[1]

Acetylimidoethyl Benzoate,  $C_6H_5C{\diagup\!\!\!\!\diagup\, NCOCH_3 \atop \diagdown\, OC_2H_5}$. — This was prepared from benzimidoethyl ester and acetyl chloride in the same manner as the above acylimido esters. The ethereal solution was washed with dilute sodium hydroxide and water.

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[1] Pinner: Ber. d. chem. Ges., **25**, 1436.

On evaporation, an oil was obtained which was distilled at 13 mm. pressure. About one-third was collected below 140°.5 and the remaining two-thirds from 140°.5 to 147°.5.

The larger portion was again distilled at 17 mm., when the greater part boiled at 151°. A nitrogen determination of this gave the following result:

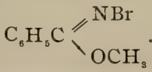
	Found.	Calculated for $C_{11}H_{13}NO_2$.
N	7.65	7.33

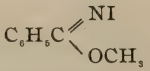
When acetylimidoethyl benzoate is treated with dilute sulphuric acid, as described in the case of the methyl compound, it is converted into acetbenzamide with evolution of heat.

Halogen Imido Esters.

The first representatives of this class of compounds in the benzoic acid series have just been prepared by Stieglitz,[1] who describes chlorimidoethyl benzoate and bromimidoethyl benzoate. He obtained these compounds by acting on the imido ester hydrochlorides with sodium hypochlorite and hypobromite. These interesting compounds were obtained as oils which in the case of the chlorine compound was found to distil unchanged at 16 mm. pressure.[2]

We have found that bromimidomethyl benzoate and the analogous iodimidomethyl ester result, along with other products, by directly combining the free esters with the halogen.

Bromimidomethyl Benzoate,  $C_6H_5C\begin{matrix}\nearrow NBr\\ \searrow OCH_3\end{matrix}$.—This was obtained as a pale yellow oil of pleasant odor, which can be distilled below 20 mm. pressure. It reacts with strong aqueous ammonia with effervescence, giving off nitrogen. Dilute hydrochloric acid evolves bromine. It is therefore identical in properties with its homologue bromimidoethyl benzoate described by Stieglitz.

Iodimidomethyl Benzoate,  $C_6H_5C\begin{matrix}\nearrow NI\\ \searrow OCH_3\end{matrix}$. — Iodine reacts with benzimidomethyl ester very slowly. After warming the mixture on the water-bath for several days the mass was extracted with ether, the ether shaken with solid potassium hydrate, and the uncombined iodine removed. On evaporating off the ether in a vacuum desiccator over potassium hydrate, the iodimidomethyl benzoate was obtained as a light yellow oil, mixed with unaltered imido ester. A small amount of colorless needles separated. They were insoluble in water and boiling alcohol. They melted from 222° to 228° and were probably triphenyltricyanide or cyaphenin. When the above oil was treated with strong ammonia it turned black from the separation of iodine. Dilute nitric acid gave the same result. On attempting to distil the crude product at 13 mm. pressure, it decomposed with the separation of iodine.

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[1] This JOURNAL, 18, 751.

[2] It is interesting to note the great stability of this substituted nitrogen chloride.

Owing to the appearance of Dr. Stieglitz's paper, and since he states his intention of further investigating these compounds, the work on the halogen imido esters has been abandoned by us at this point. We desire to reserve the work on acyl imido esters for ourselves, and, it is our intention to investigate the action of other acid chlorides on the imido esters and isoanilides, and also to examine the reactions of the acyl imido esters more thoroughly.

New Haven, November, 1896.

ON THE EFFECT OF LIGHT ON THE DISPLACEMENT OF BROMINE AND IODINE FROM ORGANIC BROMIDES AND IODIDES.

By J. H. Kastle and W. A. Beatty.

The halogen derivatives of the sulphonamides have been under investigation in this laboratory for some time. It has been found that these compounds are readily decomposed by heat and chemical reagents of various kinds. While studying their properties it occurred to one of us (Kastle) to test their behavior towards light. A small quantity of the dibrom derivative of benzenesulphonamide, $C_6H_6SO_2NBr_2$, was exposed to the sunlight in a sealed tube. After remaining exposed to the light for a short time, it was observed that decomposition of the compound had taken place, whereby a considerable quantity of bromine vapor was observed to have been set free. A small amount of the bromine compound was next placed in a tube with a small quantity of water, and the tube sealed and exposed to the sunlight. Bromine vapor again made its appearance, filling the upper part of the tube, thereby indicating that the compound had been decomposed by light even in the presence of water. The decomposition of this class of compounds by light has been found to be more deep-seated than it was at first thought to be, as the result of which this subject is still under investigation. Our study of this decomposition, however, while not complete in itself, has incidentally led to some interesting observations as to the displacement of bromine and iodine from their most stable compounds. The first clue that such displacement can be brought about was furnished by the conduct of the dichlor derivative of *p*-brombenzenesulphonamide, $BrC_6H_4.SONCl_2$, towards sunlight. This substance was placed in a tube, together with a small amount of water; the tube was then sealed, and exposed to the direct sunlight. After standing for some time it was seen that chlorine had been set free. The tube was then allowed to remain exposed to the direct sunlight for several days longer, when it was observed that bromine vapor had made its appearance in the place of chlorine. This, of course, indicated that the chlorine, after its liberation from the compound, had reacted with the substance remaining so as to set free bromine from the benzene ring. This reaction seemed so remarkable in certain respects that it was deemed expedient to make still other experiments along this line. The question of course suggested itself in this connection, could chlorine thus evolved effect the displacement of bromine or iodine in general or only from the original molecule of which it had formed a part? In order to test this point the following experiments were tried:

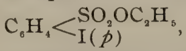
I. Benzenedibromsulphonamide and iodoform were brought together with a little water in a sealed tube and exposed to the sunlight for several days. An abundance of iodine was set free.

II. *p*-Toluenedichlorsulphonamide and iodoform gave a result similar to that obtained in I., except that the reaction took place more slowly.

III. *p*-Toluenedichlorsulphonamide and *p*-iodobenzoic sulphinide, together with water, were exposed to the light in a sealed tube from Sept. 26 to Oct. 20. The solution contained an abundance of free iodine, as was shown by its color and by filtering and shaking with carbon disulphide.

IV. *p*-Toluenedichlorsulphonamide and *p*-dibrombenzene were allowed to stand under water exposed to the sunlight from Sept. 26 to Oct. 21. After filtering the solution gave a very distinct test for bromine.

V. *p*-Toluenedichlorsulphonamide with the compound



$$C_6H_4<\begin{matrix}SO_2OC_2H_5\\ I(p)\end{matrix},$$

under water, stood in sunlight nearly all the time from Sept. 25 to Oct. 30. On Oct. 29, it was observed that the water above the insoluble ether was slightly colored. On Oct. 30 this color became very distinctly brownish yellow. The tube was opened and the contents filtered. Carbon disulphide was added to the filtrate. An excellent test for iodine was obtained. The ether that remained was colored pink.

VI. Benzenedibromsulphonamide and *p*-iodosulphinide and water were exposed to light from Nov. 3 to Nov. 11. The presence of free iodine was easily detected.

VII. Barium *p*-iodobenzenesulphonate and benzenedibromsulphonamide in water were exposed to light in a sealed tube from Nov. 3 to Nov. 11.

A test showed the presence of considerable free iodine.

The following experiments were tried in the dark.

I. *p*-Toluenedichlorsulphonamide and iodoform in a small quantity of water were kept in the dark from Sept. 25 to Nov. 19. Only a faint test for iodine was obtained.

II. *p*-Brombenzenedichlorsulphonamide in a little water was kept in the dark from Sept. 26 to Nov. 19. No test for bromine.

III. *p*-Toluenedichlorsulphonamide and dibrombenzene, in a little water, was kept in a sealed tube in the dark from Sept. 26 to Nov. 19. No test for bromine.

IV. *p*-Brombenzenedichlorsulphonamide and iodoform in a little water, were kept in the dark from Sept. 26 to Nov. 19. Good test for iodine.

It thus appears that the chlorine liberated from the dichlorsulphonamides by the action of light can displace bromine and iodine from their most stable compounds, and that the bromine of the dibromsulphonamides, when liberated, can displace iodine even from the benzene ring. Whereas in the dark, there being no liberation of the chlorine from the dichlorsulphonamide there is no displacement of the bromine or iodine from the organic halide, except from unstable compounds like iodoform; and with this substance it seems that a direct reaction takes place.

Action of Chlorine Water on Organic Bromides and Iodides.

The action of chlorine[1] water itself was next tried upon the following brom and iodo compounds; *viz.*, tetraiodopyrrol, ethyl *p*-iodobenzenesulphonate, *p*-iodobenzoic sulphinide, barium *p*-iodobenzenesulphonate, potassium *p*-brombenzenesulphonate, tribromphenol, *p*-dibrombenzene. The mode of procedure was as follows: About 0.2 gram of the iodo or brom compound was brought together in a test-tube with 5 cc. of chlorine water; the tube was then sealed and exposed to the light. Three of these tubes, *viz.*, those containing the tetraiodopyrrol, *p*-iodosulphinide, and barium *p*-iodobenzenesulphonate were exposed for nine days, from the 2nd to 11th of November. The experiment with the ethyl *p*-iodobenzenesulphonate was continued until Nov. 14, having an exposure of twelve days. That with the potassium *p*-brombenzenesulphonate was concluded on Nov. 12, having had an exposure of ten days.

In some of our experiments with tribromphenol this substance and the chlorine water were simply shaken together. Other experiments with this substance had an exposure of several hours. So with *p*-dibrombenzene, experiments with chlorine water were tried in which the exposure ranged from half an hour to several days.

These experiments were concluded by testing for bromine or iodine,[2] and, in every instance, an excellent test for either bromine or iodine was obtained, showing that chlorine in aqueous solution had effected the displacement of the bromine or iodine.

---

[1] The chlorine water used in the experiments herein described was freshly prepared for each experiment or set of experiments. Usually the solution was about $\frac{N}{10}$.

[2] The test for bromine or iodine in these and the other experiments herein described was conducted in the following manner. After the desired exposure to light, the tube was opened and its contents filtered. The filtrate was shaken with a little zinc dust and again filtered. To this filtrate there was added a little chlorine

These results certainly go to show that bromine and iodine are displaced from even their most stable organic compounds by means of chlorine in aqueous solution, even in the case of compounds, which are practically insoluble in water. The ease with which this displacement takes place varies of course, and that too very considerably, with the nature of the iodo or brom derivatives. With compounds, such as propyl iodide, tribromphenol, etc., it was only necessary to shake the compound with chlorine water in order to have the setting free of iodine or bromine begin at once. Others, such as the ethyl *p*-iodobenzenesulphonate, seemed to require prolonged action of the chlorine before the iodine made its appearance.

On the Effect of Light upon the Reaction between Chlorine with Water and Organic Halides.

Still more remarkable is the effect of light upon the reaction. This effect is noticeable with the *p*-iodobenzoic sulphinide. After nine days the tube containing this compound and the chlorine water, which had been exposed to the sunlight, gave a very distinct test for iodine; whereas, a second tube, exactly like the first in contents, but which had been kept in the dark, showed at the best but a very faint trace of iodine.

The effect of light is still better shown in the experiments with *p*-dibrombenzene and chlorine water. In one of our earlier experiments along this line, two sealed tubes were prepared, each containing about 0.1 gram dibrombenzene and 5 cc. chlorine water. One of these was exposed to the light and kept immersed in running water, the temperature of which was 11°.5 to 13°.5 C. The other tube was kept in the dark. At the end of four hours the tubes were opened, their contents fil-

water or *p*-toluenedichlorsulphonamide[2] and carbon bisulphide. If, under these conditions, either the color of bromine or iodine was imparted to the carbon bisulphide it indicated that the displacement of one or the other of these halogens had been effected.

[2] The use of *p*-toluenedichlorsulphonamide in this connection is similar to that of benzenedichlorsulphonamide, which has been proposed as a reagent for bromine and iodine.

tered, and the filtrates tested for bromine. The one that had been exposed to the light gave a very distinct test for bromine, whereas, that which had remained in the dark showed no traces of bromine. The day on which these experiments were tried was alternately fair and cloudy, but mostly cloudy, so that the tube exposed to the light was in only diffused light during the greater part of the time, and yet this was sufficient to cause the decomposition. Still more conclusive results were obtained in a series of experiments begun Nov. 10, at 2.45 P.M., and conducted as follows: 0.2 gram dibrombenzene, together with 10 cc. chlorine water, were placed in a small glass-stoppered bottle. Six of these bottles having been thus prepared, three of them were placed in the direct sunlight and three kept in the dark. On Nov. 11, at 2.30 P. M., one of the bottles which had been exposed to the light was compared with one of those which had been kept in the dark. The difference was easily seen. The liquid in the bottle which had been exposed to the light was decidedly yellow, and a small quantity of yellowish-red vapor filled the upper part of the bottle. After filtering, the liquid gave an abundant test for bromine. On the other hand, the liquid in the bottle which had been kept in the dark was colorless, with not a trace of yellowish-brown vapor in the upper part of the bottle, and when tested for bromine it gave only a trace. In order to make sure of this point another one of the bottles which had been kept in the dark was opened and tested for bromine, with like result. It should be remarked, further, in this connection, that the afternoon of Nov. 10 was cloudy during the greater part of the time, and that Nov. 11 was also cloudy, so that the exposure to direct sunlight was short. Of the two bottles which were left exposed to the light at the conclusion of the first test, one was broken by accident, the third bottle was left exposed until Nov. 12, at 3.30, when this series of experiments was completed. At 3.30, Nov. 12, the bottle which had been exposed to the light since Nov. 10, 2.45 P.M., was compared with the bottle which had been kept in the dark since that time. The difference was very striking. The liquid in the bottle which had been exposed to the light was distinctly yellowish-red and vapors of bromine filled the upper part of the bottle. In fact, bromine was so abundant as to need no test to confirm its presence. In the bottle which had been kept in the dark the liquid was as colorless as water. No bromine vapor could be seen in the bottle, and when its contents were filtered and tested, they gave only the slightest traces of bromine.

By reference to the record of the weather,[1] which was kept during this time, it will be observed that even this bottle, which was exposed to the light for the longest period, was in the direct sunlight only during the last day of exposure. In order to determine whether it was the heat or the light of the direct sunlight that caused the acceleration in the action of chlorine water on *p*-dibrombenzene, a tube containing 0.2 gram of the dibrombenzene and 5 cc. of chlorine water was immersed in running water, the temperature of which varied from 14° to 18° C., and was exposed to the direct sunlight for six hours. At the end of this time it could be easily observed that the reaction had taken place. The liquid in the tube had a decided yellowish-red color, and on being filtered and shaken with carbon bisulphide it gave an abundant test for bromine. This shows that the sunlight at 14°–18° C. is capable of working this change. In order, further, to make sure of the effect of an increase in temperature on the progress of the reaction, a tube containing the same quantities of dibrombenzene and chlorine water was exposed to the temperature of 50° C. in the dark, for five hours. When examined at the end of this time the liquid in the tube was seen to be colorless, and on filtering and testing for bromine it gave no test for this element. A similar tube was exposed to a temperature of 100° C., for five hours. After heating for this length of time it was allowed to remain in the dark all night at the ordinary temperature. When examined, it was found that the liquid in the tube was reddish-yellow. After filtering, the filtrate gave a splendid test for bromine. All these results, together with that described above, go to show that at ordinary temperature, and even up to 50° C., the reaction is not so much dependent on heat as it is on light. This, of course, does not mean that the reaction in question is uninfluenced by temperature. As a matter of fact, it has been observed that the reaction proceeds more rapidly at 30° C. in the sunlight than at 14° C, and, as has just been described, at 100° C. the action of the chlorine on the dibrombenzene takes place in the absence of light altogether. What is meant, rather, is that at ordinary temperatures light exerts an accelerating influence on the course of the reaction.

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[1] Record of weather for November, up to the time of writing:

Nov. 1, Fair.
" 2, Fair.
" 3, Partly cloudy.
" 4, Cloudy.
" 5, "
" 6, Fair.
" 7, Cloudy.
" 8, "
" 9, Partly cloudy.
" 10, Cloudy during greater part of day.

Nov. 11, Cloudy.
" 12, Fair.
" 13, "
" 14, Partly cloudy.
" 15, Fair.
" 16, "
" 17, Cloudy.
" 18, Partly cloudy.
" 19, Cloudy.
" 20, "

The last of the experiments herein described, involving exposure to light, was concluded on the 17th inst.

Still another experiment was tried, as follows, with the view of finding whether the chlorine actually replaced the bromine: 1 gram of pure dibrombenzene was placed in a small Florence flask, together with 100 cc. of chlorine water, containing 0.0057 gram chlorine per cc., or about twice the quantity required completely to displace the bromine from the dibrombenzene. The flask was then sealed and placed in the sunlight at 2.25 P.M., Nov. 6. The sun shone brightly during the entire afternoon. About an hour and a half after the beginning of the exposure to the sunlight, it could be clearly seen that some change was taking place. The liquid above the dibrombenzene was distinctly darker and of a more decided yellowish tint. Nov. 7 and 8 it was kept in one of the laboratory closets, and no further change in the color was observable. On Nov. 9 it was exposed to the light all day. It was very cloudy during the entire day and little if any change could be noted. It was also exposed all day on Nov. 10 and 11, both of which days were cloudy, except for a little while during the afternoon of the 10th. It could be seen, however, that the liquid had darkened a little in color. On the 12th the sun came out about 10.30, and shone brightly the rest of the day. During the first hour's exposure to the sunlight on this date it looked as if as great a change had taken place as had occurred during all the preceding days of exposure. Vapor of bromine could be seen in the upper part of the flask. Nov. 13 was a fair day, the sun shining brightly during the entire day. This day's exposure seemed to complete the change, so far at least as the replacement of the bromine by the chlorine was concerned. The liquid in the flask had about the color of strong bromine water, and the upper part of the flask seemed saturated with bromine vapor. We allowed the flask to remain exposed to the light until the 17th. During the interval between the 13th and 17th about the only change observable was that the red color of the bromine became lighter, owing, doubtless, to its reacting with the water to form hydrobromic acid. On the 17th the flask was opened and its contents filtered. The filtrate was evaporated to dryness. Only a very small amount of solid residue was left, and this was not further examined. The white crystalline residue obtained on filtration was dried and weighed. It was found to weigh 0.6400 gram. The quantity of dichlorbenzene, which would be found if all the dibrombenzene were thus transferred is 0.6228 gram. The melting-point of the residue was found to be 55°–57°; that of dichlorbenzene is given as 55–56°.5. The residue was recrystallized from ether. The recrystallized product was not found to melt sharply, the melting-point being from 62°–66° C. The remainder of the substance was fused with a mixture of sodium carbonate and potassium nitrate. The fused mass was dissolved in water and the solution boiled with zinc dust. This was then filtered, and to the clear solution silver nitrate and nitric acid were added. The precipitate formed was shown to be a mixture of silver bromide and silver chloride. Hence the crystalline residue which is left after exposing *p*-brombenzene and chlorine water to the sunlight is either a mixture of *p*-chlor- and *p*-brombenzene or *p*-chlorbrombenzene, C_6H_4ClBr, a compound obtained by Körner[1] by the action of bromine on chlorbenzene, which is described as melting at 67° C.

Further work with larger quantities of material will be necessary definitely to settle this point. One thing, however, seems absolutely certain, and that is that some chlorine derivative is formed by the action of chlorine water in the sunlight on *p*-dibrombenzene, and that large quantities of bromine are set free. It seems probable that the chlorine not only displaces but replaces bromine and iodine in their aromatic derivatives.

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[1] J., 1875, 319.

It is believed that these results are new, especially those showing the accelerating influence of light upon the progress of the reactions studied.

No systematic study of the displacement of one halogen by another in organic compounds seems to have been made, and only a few scattering observations bearing upon this subject are to be found in the literature.

Dumas and Stas[1] have observed that chlorine gas acting on ethyl iodide gave ethyl chloride and free iodine. Geuther[2] has shown that ethyl iodide is converted into ethyl chloride by iodine chloride. Willgerodt[3] has shown that the compounds $C_6H_4Br.I.Cl_2$ and $C_6H_5ICl_2$ decompose alcoholic iodides with the setting free of iodine. Löscher[4] has observed that iodoform is changed to bromoform by the action of bromine. Then in the last edition of Watts' Dictionary, Vol. III, p. 31, is to be found the statement under the general remarks about iodo compounds that chlorine and bromine replace iodine directly.

Further, R. Meyer[5] has made the interesting observation that whereas chlorine and bromine replace iodine in isopropyl iodide yielding isopropyl chloride and bromide, respectively, *chlorine does not replace bromine in isopropyl bromide*. It is to be observed in this connection that R. Meyer allowed chlorine gas and pure bromine to act upon the organic halide in the dry state. It is conceivable, of course, that chlorine in aqueous solution and in the sunlight might be found to act more energetically upon this bromine derivative, a point which we hope to investigate as soon as possible.

It will be observed, therefore, that the results herein described are somewhat different from any that have ever been

[1] Ann. Chem. (Liebig), **35**, 162.

[2] *Ibid*, **123**, 123.

[3] J. prakt. Chem., [2], **33**, 154–158.

[4] Ber. d. chem. Ges., **21**, 410.

[5] J. prakt. Chem., [2]. **34**, 104.

obtained, and it is believed that they are of sufficient interest to warrant publication in their present form. Still further work is now in progress along this line.

State College of Kentucky,
Lexington, November, 1895.

THE SPECIFIC GRAVITIES OF WATER SOLUTIONS OF FORMIC ACID.

By George M. Richardson and Pierre Allaire.

Having frequent occasion to determine the approximate amount of acid in formic acid solutions, we have prepared the following table. The specific gravities were determined by the use of a picnometer at 20° C. The amount of acid in the various solutions was determined by titrating with a standard solution of sodium hydroxide, with phenolphthaleïn as an indicator. Pure anhydrous formic acid was prepared in the usual manner from recrystallized lead formate and dry hydrogen sulphide, and the acid thus obtained was redistilled over dry lead formate. Formic acid was finally obtained which gave 100 per cent. acid upon titration with the standard alkali. This acid was found to have a specific gravity of 1.2213 at 20° C. (water at 4° C. = 1). The anhydrous acid was then diluted by the addition of measured amounts of distilled water, the specific gravity and the amount of acid in each solution being determined. In this manner seventy-one determinations were made at regular intervals between the pure acid and a dilute solution containing only 0.618 per cent. acid.

From the data thus obtained the following table was calculated :

Specific Gravities of Mixtures of Formic Acid and Water at 20° C. Water at 4° C. = 1.

Specific gravity of mixture.	Per cent. of formic acid by weight.	Per cent. of formic acid by volume.	Specific gravity of mixture.	Per cent. of formic acid by weight.	Per cent. of formic acid by volume.
0.9983	0.00	0.00	1.0941	39.00	34.92
1.0020	1.00	0.82	1.0964	40.00	35.90
1.0045	2.00	1.64	1.0991	41.00	36.88
1.0071	3.00	2.48	1.1016	42.00	37.89
1.0094	4.00	3.30	1.1039	43.00	38.85
1.0116	5.00	4.14	1.1063	44.00	39.86
1.0142	6.00	4.98	1.1086	45.00	40.82
1.0171	7.00	5.81	1.1109	46.00	41.83
1.0197	8.00	6.68	1.1131	47.00	42.82
1.0222	9.00	7.55	1.1158	48.00	43.88
1.0247	10.00	8.40	1.1186	49.00	44.91
1.0272	11.00	9.26	1.1208	50.00	45.88
1.0297	12.00	10.14	1.1224	51.00	46.87
1.0322	13.00	11.03	1.1245	52.00	47.89
1.0346	14.00	11.96	1.1270	53.00	48.93
1.0371	15.00	12.80	1.1296	54.00	49.97
1.0394	16.00	13.68	1.1321	55.00	51.01
1.0418	17.00	14.48	1.1343	56.00	52.02
1.0442	18.00	15.38	1.1362	57.00	53.04
1.0465	19.00	16.29	1.1382	58.00	54.07
1.0489	20.00	17.17	1.1402	59.00	55.09
1.0513	21.00	18.06	1.1425	60.00	56.13
1.0538	22.00	18.97	1.1449	61.00	57.16
1.0562	23.00	19.88	1.1474	62.00	58.26
1.0586	24.00	20.81	1.1494	63.00	59.30
1.0610	25.00	21.73	1.1518	64.00	60.35
1.0634	26.00	22.63	1.1544	65.00	61.44
1.0657	27.00	23.53	1.1566	66.00	62.51
1.0682	28.00	24.47	1.1585	67.00	63.57
1.0706	29.00	25.42	1.1605	68.00	64.62
1.0730	30.00	26.37	1.1629	69.00	65.71
1.0754	31.00	27.28	1.1656	70.00	66.80
1.0778	32.00	28.20	1.1678	71.00	67.90
1.0801	33.00	29.19	1.1703	72.00	68.99
1.0824	34.00	30.13	1.1729	73.00	70.10
1.0848	35.00	31.10	1.1753	74.00	71.21
1.0872	36.00	32.05	1.1770	75.00	72.27
1.0896	37.00	32.98	1.1786	76.00	73.34
1.0920	38.00	33.97	1.1802	77.00	74.38

Specific gravity of mixture.	Per cent. of formic acid by weight.	Per cent. of formic acid by volume.	Specific gravity of mixture.	Per cent. of formic acid by weight.	Per cent. of formic acid by volume.
1.1819	78.00	75.47	1.2045	90.00	88.74
1.1838	79.00	76.58	1.2060	91.00	89.84
1.1861	80.00	77.67	1.2079	92.00	91.00
1.1877	81.00	78.81	1.2100	93.00	92.13
1.1897	82.00	79.92	1.2118	94.00	93.22
1.1915	83.00	80.97	1.2141	95.00	94.48
1.1930	84.00	82.06	1.2159	96.00	95.57
1.1954	85.00	83.19	1.2171	97.00	96.63
1.1977	86.00	84.32	1.2184	98.00	97.76
1.1995	87.00	85.45	1.2203	99.00	98.93
1.2013	88.00	86.54	1.2213	100.00	100.00
1.2029	89.00	87.64			

Some idea of the contraction in volume that takes place when formic acid and water are mixed may be gained from the following table.

The first column gives the per cent. by weight of acid in the mixture; the second column gives the actual specific gravity of the mixture; the third column gives the specific gravity such a mixture would have were there no change in volume; the fourth column gives, in cubic centimeters, the contraction that takes place when enough anhydrous acid and water are brought together to make 100 cc. of the mixture.

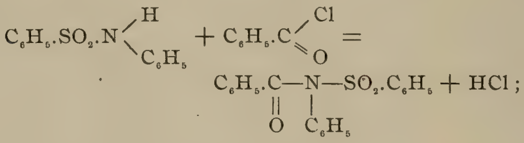
Per cent. by weight of formic acid in mixture.	Actual specific gravity of mixture.	Calculated specific gravity if no volume change.	Contraction in cc.
10.00	1.0247	1.0168	0.78
20.00	1.0489	1.0361	1.23
30.00	1.0730	1.0561	1.60
40.00	1.0964	1.0769	1.81
50.00	1.1208	1.0986	2.02
60.00	1.1425	1.1211	1.90
70.00	1.1656	1.1446	1.83
80.00	1.1861	1.1691	1.45
90.00	1.2045	1.1946	0.82

STANFORD UNIVERSITY, CAL.,
JUNE 23, 1896.

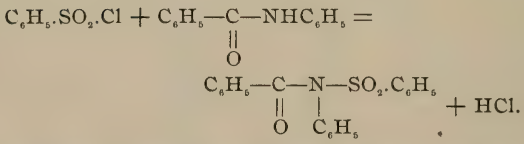
THE CONSTITUTION OF BENZANILIDE.

By N. Knight.

The uncertainty in regard to the constitution of benzanilide suggested the experiments described in this paper. Lack of time prevented me from pursuing the investigation farther than herein indicated and, although the results do not justify the drawing of any important conclusion in regard to the constitution of benzanilide, they are of some interest, and may be of service to some future investigator. Just as benzamide may have the structure $C_6H_5.C\begin{smallmatrix}\diagup NH_2\\ \diagdown O\end{smallmatrix}$ or $C_6H_5.C\begin{smallmatrix}\diagup OH\\ \diagdown NH\end{smallmatrix}$, so the anilide may have the structure, $C_6H_5.C\begin{smallmatrix}\diagup NHC_6H_5\\ \diagdown O\end{smallmatrix}$, or $C_6H_5.C\begin{smallmatrix}\diagup OH\\ \diagdown NC_6H_5\end{smallmatrix}$. If the first of these two formulas is correct, then, apparently, the same product should result whether the sulphanilide is treated with benzoyl chloride, or benzanilide is treated with benzenesulphonchloride :

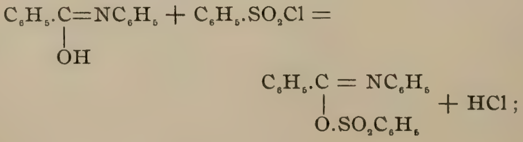
1.


$$C_6H_5.SO_2.N\begin{smallmatrix}\diagup H\\ \diagdown C_6H_5\end{smallmatrix} + C_6H_5.C\begin{smallmatrix}\diagup Cl\\ \diagdown O\end{smallmatrix} = \underset{\displaystyle O}{\overset{}{C_6H_5.\underset{\|}{C}}}\!-\!\underset{\displaystyle C_6H_5}{\underset{|}{N}}\!-\!SO_2.C_6H_5 + HCl;$$

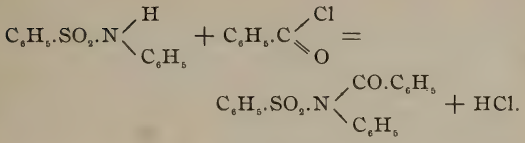
2.


$$C_6H_5.SO_2.Cl + C_6H_5\!-\!\underset{\displaystyle O}{\underset{\|}{C}}\!-\!NHC_6H_5 = C_6H_5\!-\!\underset{\displaystyle O}{\underset{\|}{C}}\!-\!\underset{\displaystyle C_6H_5}{\underset{|}{N}}\!-\!SO_2.C_6H_5 + HCl.$$

If the second formula above given for benzanilide is correct, then the products formed in these reactions should apparently be different :

1.


$$C_6H_5.\underset{\displaystyle OH}{\underset{|}{C}}{=}NC_6H_5 + C_6H_5.SO_2Cl = C_6H_5.\underset{\displaystyle O.SO_2C_6H_5}{\underset{|}{C}} = NC_6H_5 + HCl;$$

2. 

$$C_6H_5.SO_2.N\begin{cases}H\\C_6H_5\end{cases} + C_6H_5.C\begin{cases}Cl\\O\end{cases} = C_6H_5.SO_2.N\begin{cases}CO.C_6H_5\\C_6H_5\end{cases} + HCl.$$

So much for speculation. As a matter of fact the reactions do not take place as it was thought they might.

Twelve grams benzenesulphanilide was mixed with 8 grams benzoyl chloride and the mixture in a test-tube immersed in a sulphuric-acid bath, the temperature of which was gradually raised. At 110° there was a copious evolution of hydrochloric acid, which ceased at 140°. The mixture was further heated to 180°, and kept at that temperature for ten hours. The cooled mass was a red, brittle solid of vitreous luster, breaking with a conchoidal fracture. It was easily soluble in dilute alcohol. By dissolving in alcohol and adding water in sufficient quantity, there separated from the solution a reddish, thick, oily substance, which was easily removed. On standing a few days, a white substance crystallized from the solution. This was purified by repeated crystallizations from alcohol, and was found to melt at 151°. Attempts to purify the oily portions were fruitless. The crystals were analyzed with the following results, which show that the substance is dibenzoylanilide, $\begin{matrix}C_6H_5CO\\C_6H_5CO\end{matrix}>NC_6H_5$:

	Calculated for $C_{20}H_{15}NO_2$.	Found.	
		I.	II.
C	79.73	80.19	80.01
H	4.98	5.17	5.15
N	4.65	4.41	4.48

There is some uncertainty as regards the true melting-point of dibenzoylanilide, as different experimenters give different points. A consideration of the properties of the substance and of the results obtained by analyzing it, leave little doubt in regard to its identity. How it can be formed under the conditions described is another question. This will be briefly discussed farther on.

Reversing the order, 9 grams benzenesulphonchloride was mixed with 8.5 grams benzanilide, and the mixture heated as in the first experiment. In general, the same phenomena were observed, and a similar reddish solid was formed. This was treated with alcohol and water, and a white, crystalline substance was obtained. This, like the substance obtained in the first experiment, melted at 151°, and the analysis showed that it had the same composition.

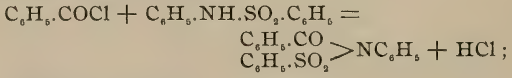
In both experiments a second compound was obtained, which, on purification, proved to be the aniline salt of benzenesulphonic acid, $C_6H_5.SO_2ONH_3C_6H_5$. It appeared in the form of beautiful white crystals, which melted at 231°, and, on analysis, gave the following results :

	Calculated for $C_{12}H_{13}SNO_3$.	Found. I.	II.
C	57.37	57.58	57.28
H	5.18	4.83	....
S	12.75	....	....
N	5.58	....	....

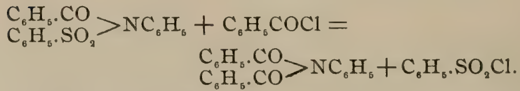
The salt was prepared by bringing benzenesulphonic acid and aniline together, and it was found to be identical with that obtained as above indicated.

Other by-products were formed in both experiments, but in quantities insufficient for a satisfactory examination. The most definite of these was a substance crystallizing in plates, that melted at 212°. It was not always observed.

How can dibenzoylanilide be formed in the experiments described? It seems possible that in the first experiment the principal reactions are these :

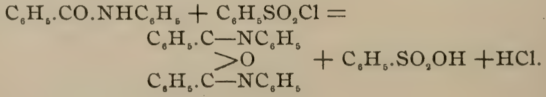
1.


$$C_6H_5.COCl + C_6H_5.NH.SO_2.C_6H_5 = \left.\begin{matrix} C_6H_5.CO \\ C_6H_5.SO_2 \end{matrix}\right> NC_6H_5 + HCl;$$

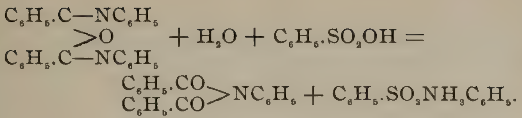
2.


$$\left.\begin{matrix} C_6H_5.CO \\ C_6H_5.SO_2 \end{matrix}\right> NC_6H_5 + C_6H_5COCl = \left.\begin{matrix} C_6H_5.CO \\ C_6H_5.CO \end{matrix}\right> NC_6H_5 + C_6H_5.SO_2Cl.$$

In the second experiment the principal changes may be those represented below :

1.


$$C_6H_5.CO.NHC_6H_5 + C_6H_5SO_2Cl = \begin{matrix} C_6H_5.C{-}NC_6H_5 \\ \quad >O \\ C_6H_5.C{-}NC_6H_5 \end{matrix} + C_6H_5.SO_2OH + HCl.$$

2. 

$$\begin{matrix}C_6H_5.C—NC_6H_5\\ \quad >O\\ C_6H_5.C—NC_6H_5\end{matrix} + H_2O + C_6H_5.SO_2OH = \begin{matrix}C_6H_5.CO\\ C_6H_5.CO\end{matrix}>NC_6H_5 + C_6H_5.SO_3NH_3C_6H_5.$$

REVIEWS.

TRAITÈ DE CHIMIE ORGANIQUE D'APRÈS LES THÈORIES MODERNES: par AUGUSTE BÈHAL, Professeur agrégé à l'École supérieure de Pharmacie de Paris, Pharmacien en chef de l'Hôpital Ricord, Lauréat de l'Institut, Secrétaire général de la Société chimique, etc. Précéde d'une Préface de M. CH. FRIEDEL, Membre de l'Institut. Tome Premier, avec 36 Figures dans le Texte. Paris: Octave Doin, Éditeur. 1896. 963 pp. Price, 30 francs ($6.00).

This book has been honored by special mention in a recent meeting of the German Chemical Society, a fact which will no doubt attract much attention to it. That Professor Friedel has been willing to write a preface for it is additional evidence in its favor. To be sure this preface consists mostly of a reply to Ostwald's article on Atoms, that stirred up the physicists and chemists so deeply last year, but what M. Friedel says of M. Béhal's book is most complimentary: "Ceux qui liront le livre que j'ai l'honneur de présenter au public, et qui se recommande par luimême, étant le rêsultat d'un enseignement de six années fait à l'École supérieure de pharmacie de Paris, comprendront facilement combien il serait vain et illusoire de supprimer les hypothèses et les symboles qui servent en chimie à enchaîner les faits, à représenter les transformations, à soutenir la mémoire sans mettre à leur place quelque chose de plus satisfaisant. Ces hypothèses et ces symboles ont été et sont chaque jour des guides fidèles dans la découverte de faits nouveaux, et personne ne pourrait contester l'action puissante qu'ils ont exercée pour le progrès de la chimie.

"M. Bêhal, qui a eu le mérite d'introduire le premier la notation et, ce qui vaut mieux, les idées atomiques dans l'enseignement de l'École de pharmacie, et qui est non seulement un professeur plein d'entrain mais un chercheur habile et heureux, a su donner à son livre ce double caractère theorique et pratique."

The chief characteristic of the book is its clear systematic arrangement. Nothing could be better. The text is also clear, readable, and interesting. It is difficult, however, to see to what class of students the book is addressed. It cannot be intended for beginners, for the first 200 pages deal with matters that cannot be understood until some knowledge of the compounds of carbon has been acquired. On the other hand, the accounts of methods of determining constitution are often so detailed and elementary as to indicate that they cannot be intended for advanced students. The book is, in fact, of intermediate grade, and is well calculated to be of assistance to those who have already studied organic chemistry to some extent. A feature of the book that will commend it to some is the use of the new nomenclature adopted by the Geneva Congress in 1892. There is no other book except Beilstein in which the new nomenclature is used systematically, and yet, judging by the recent numbers of the journals of chemistry, it is time that chemists should familiarize themselves with it, as it is certainly coming into more and more common use. We English-speaking chemists are going to have a hard time of it with the suffixes *ane*, *ene*, and *ine*. We can't pronounce *ene* āne without running afoul of *ane*, nor can we pronounce it ean without danger of confusion with *ine*. We might, to be sure, give *ine* the long ī, but that is not in accordance with custom. There are difficulties in the way, plainly.

References to the journals of chemistry are rarely given, though the names of chemists are frequently given. French names predominate. They are often given when the relative importance of the subjects does not appear to call for their mention. On the other hand, great names are omitted in some cases. For example, Bunsen is not mentioned in connection with cacodyl compounds, while Meunier, Bourquelot, Villiers and Fayolle, Jungfleisch, Maquenne, and other French names are found at every turn. This is, in a way, a small matter, and does not to any extent lessen the value of the book, which may be cordially recommended to American students. I. R.

ANALYTICAL CHEMISTRY. By N. MENSCHUTKIN, Professor in the University of St. Petersburg. Translated from the third German edition under the supervision of the author, by JAMES LOCKE. Part I, Qualitative Analysis. New York: MacMillan. 1896. 294 pp.

Menschutkin's is perhaps the best in every respect of the larger text-books on this subject. It is certainly the best for study. The general discussions of reactions of groups of elements, and the study of single elements, make everything clear and logical to the student who has learned to think chemically, and it is intended only for such. The author rightly protests against teaching analysis to those who have not studied general chemistry. Qualitative analysis becomes clear and interesting under Menschutkin's guidance, and the translation, which is good, should be welcomed. E. R.

RECHERCHES SUR LA CONGELATION DES SOLUTIONS AQUEUSES ÉTENDUES. Par M. A. PONSOT, ancien élère de l'École normale speciale, Agrégé de l'enseignement secondaire spécial, Docteur ès-sciences. Gauthier-Villars et Fils. Paris. 1896. pp. 114.

In the first chapter of this book the author has given a brief review of the work which has been done on the lowering of the freezing-point of a solvent by the dissolved substance. The Law of Blagden, the work of Rüdorff, Coppet, and especially that of Raoult, are considered. The paper of van't Hoff, showing the analogies between dilute solutions and gases, is discussed, and its relation to the Arrhenius theory of electrolytic dissociation referred to; a theory which the author thinks is by no means supported by the experimental results.

Ponsot then takes up his own experimental investigations along this line, which consist in determining, by a new method, the lowering of the freezing-point of water, produced by solutions of sodium chloride, potassium chloride, barium chloride, calcium chloride, potassium sulphate, sulphuric acid, lead acetate, cane sugar, acetic and oxalic acids. He compares his own results in each case with those of the other investigators who have worked on these same substances, by means of curves. The *source of error* in the work of *all* the other experimenters is pointed out with not a little confidence.

Arrhenius' results are too large because his freezing-mixture was too cold. Raoult found lowerings which were too great because his refrigerating-bath was also too cold, and radiation was not entirely prevented. Jones's results are apparently affected by the same source of error. In the work of Loomis radiation came into play and affected his results considerably. The correction, which Nernst and Abegg applied, makes their results more nearly coincident with the true values, which are those found by Ponsot.

Perhaps the most interesting part of the second half of the book, which is theoretical, is that which deals with the theory of electrolytic dissociation. If this theory is true, electrolytes, at extreme dilutions, must be completely broken down into their ions. These would then lower the freezing-point of the solvent to the same extent. We have not enough data to decide whether the first point is true, but the work of Ponsot has shown that the limit of the molecular-lowering varies with the substance employed, and therefore the Arrhenius' theory of electrolytic dissociation must be abandoned. It is a matter of deep regret that Ponsot did not inform himself a little more carefully in reference to some of the experimentally established facts. On page 10 we learn that "the values of i obtained from the freezing-point method, and from conductivity are of the same order of magnitude, but coincide rarely. For the substances which Arrhenius calls regular these differences may become 15 to 20 per cent; for the others, 70 to 80 per cent." This is used as an argument against the dissociation theory. Had Ponsot consulted the recent work of Jones[1] he would have found that these differences are, in general, somewhat smaller. Below are given a few of the values of the dissociation of different types of electrolytes as calculated from the freezing-point results of Jones, and from the conductivity determinations of Kohlrausch. The dissociation coefficient α, as calculated from freezing-point lowerings is equal to $i—1$ for binary electrolytes, and $\frac{i—1}{2}$, for ternary. The well-known method of calculating α from conductivity results is $\alpha = \frac{\mu_v}{\mu_\infty}$, in which μ_v is the molecular conductivity at volume v, and μ_∞ at infinite dilution.

Compounds.	Concentration. Gram-molecular, normal.	Kohlrausch's results from conducticity. Per cent.	Jones's results from freezing-point lowerings. Per cent.
$NaCl, \mu_\infty = 1029$	0.001	98.0	98.4
"	0.01	93.5	90.5
"	0.1	84.1	84.1
$BaCl_2, \mu_\infty = 1144$	0.001	93.9	94.2
"	0.005	87.9	87.6
"	0.05	75.3	77.7
$H_2SO_4, \mu_\infty = 3342$	0.003	89.8	86.0
"	0.005	85.4	83.8
"	0.05	62.3	60.7
$NaOH, \mu_\infty = 1880$	0.002	98.9	98.4
"	0.01	99.5	93.7
"	0.05	90.4	88.4

Reference to the original paper will show that the comparison from which the above table was taken, was made for seven salts, four acids, and three bases, with results nearly as concordant throughout as the above. In the light of these facts, the full significance of the point raised by Ponsot is not quite apparent.

The question of the effect of radiation seems to have been settled satisfactorily by Raoult,[2] with the result that in the form of apparatus ordinarily employed, it is too small to consider. So much the more could it be left out of account, where the volume of the solution was large, which was true for the first time in the apparatus employed by Jones.

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[1] Phil. Mag. [5], **36**, 483.

[2] Revue Scientifique, (Paris), 1894, **2**, 321

But the objection offered by Ponsot to the dissociation theory, which it is most difficult to understand, is the last named, that the molecular-lowering at great dilution should be a constant for different substances. This would be true, in terms of the dissociation theory, only when the molecules of the different compounds dissociated into the same number of ions. The experimental work of Ponsot does not appear to bear very strongly upon this point, for the obvious reason that *he has not worked at all with very dilute solutions.*

Reference to the work of Kohlrausch[1] on conductivity, or of Jones[2] on freezing-point lowerings, will show that many of the electrolytes which Ponsot employed are not completely dissociated at the greatest dilution with which he worked. The theory of dissociation seems thus to be taxed beyond its legitimate obligations.

Were complete references to the literature given in the text itself, instead of a very imperfect list at the end of the volume, the convenience of the reader would have been met rather more satisfactorily.

Finally, since the dissociation theory must now be relegated to history, it is at least unfortunate that Ponsot did not explain why the molecular-lowering, calculated from his own results, increases with the dilution; for potassium sulphate from 4.141 to 4.624, for sulphuric acid from 4.183 to 4.576, and for lead acetate from 3.708 to 4.608. HARRY C. JONES.

KURZES LEHRBUCH DER ORGANISCHEN CHEMIE von Professor DR. A. BERNTHSEN, Vorstand des Hauptlaboratoriums der Badischen Anilin- und Soda-Fabrik, Ludwigshafen am Rhein, früher Professor an der Universität zu Heidelberg. Sechste Auflage, bearbeitet in Gemeinschaft mit DR. EDWARD BUCHNER, Professor an der Universität zu Tübingen. Braunschweig: Druck and Verlag von Friedrich Vieweg und Sohn. 1896.

The second edition of the English translation of this excellent book has already been recently reviewed in This JOURNAL (**17**, 204), so that it will only be necessary here to call attention to the changes and improvements made in this edition of the work.

The high character of the previous editions has been maintained, and the author is to be congratulated in having associated with himself in the revision of the book such an experienced teacher as Professor Buchner, of the University of Tübingen. Corrections and additions have been made, where they were necessary, to bring the book up to date, and in some cases this has necessitated a complete revision of a few chapters, like those on the acid derivatives, the sugars, the terpenes, etc. All of the excellent features of the former editions have been retained in this edition, and a much fuller and better index has been specially prepared for it by Herr Dinard.

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[1] Ann. der Phys. Wied., **26**, 161.

[2] Ztschr. phys. Chem., **11**, 110, 529; **12**, 623.

The book is almost universally used throughout Germany by those studying organic chemistry, and its popularity is attested by the fact that it has already gone through six editions in nine years. It contains just what a student of the subject wants to know without being either too full or too brief. The most recent work on the various subjects is given together with the latest theoretical views, but in every case the evidence on which these views is based is also given.

As a text-book of organic chemistry there is no book to compare with it, though it must be said that it is too full to put into the hands of beginners in the subject. For those, who already have some knowledge of organic chemistry, and who wish to supplement this knowledge and to know the latest development of the science, this book will undoubtedly be most valuable. W. R. O.

STUDIES IN CHEMICAL DYNAMICS. By J. H. VAN 'T HOFF. Revised and enlarged by DR. ERNST COHEN. Translated by THOMAS EWAN, M.Sc., Ph.D. Easton: Chemical Publishing Co.; and London: Williams & Norgate. 286 pp. 8 vo.

The appearance of this new revised and enlarged edition of van 't Hoff's *Etudes de Dynamique Chimique*, and of its English translation may well be subjects of congratulation to every one interested in the progress of general chemistry. The work still retains the form of the original edition and contains almost all of the material presented in it. It has been extended mainly by the inclusion of the numerous recent investigations carried out in van 't Hoff's laboratory, so that, as stated in the preface, it is a historical record of the work done in that laboratory. It possesses, therefore, rather the character of a scientific monograph than that of an introductory text-book; and, when used for purposes of instruction, the fact should be borne in mind that there are some important principles in regard to chemical change and equilibrium, and many important applications which are not considered in this work. As examples of these may be mentioned catalytic actions and the numerous applications of the electrolytic dissociation theory to the phenomena of equilibrium.

The book is, however, especially valuable as an original contribution to science and as an aid to the scientific investigator, for the results of many hitherto unpublished researches are presented in it, and most of the matters considered are treated in much detail. About one-half of the book is devoted to the laws governing the rate of chemical change, and the remaining half to a discussion of chemical equilibrium and of the measurement of chemical affinity. The most important additions of a general character to the original edition are a table of experiments illustrating the remarkable principle, recently discovered, that the effect of temperature on the speed of all reactions is of the same order of magnitude, a deduction of the thermo-dynamical relation between temperature and the equilibrium constant, and a detailed discussion of the methods of determining the transition temperature.

A. A. NOYES.

THE CHEMICAL ANALYSIS OF IRON.—A Complete Account of all the best known methods for the Analysis of Iron, Steel, Pig-Iron, Iron Ore, Limestone, Slag, Clay, Sand, Coal, Coke, and Furnace and Producer Gases. By ANDREW ALEXANDER BLAIR. Third Edition. Philadelphia: J. B. Lippincott Co. 1896.

The favor with which Blair's Chemical Analysis of Iron was received when the first edition was published eight years ago was due to the fact that the methods of analysis described in the book were largely the result of the actual experience of a chemist of extensive practice in this special line of work. The directions were minute, so that no one need go astray in his work, and they bore, moreover, the distinct stamp of the author's personality.

In the subsequent editions of the book the author has kept well within the bounds originally established in the first edition and has not attempted to give all the new iron and steel processes which have been proposed during recent years. If he had done this his book would have become unwieldy in size and lost much of its usefulness in losing its strong individuality. The third edition contains, in addition to minor changes in the direction of greater accuracy, a few new and approved processes, and also the preliminary report of the Subcommittee on Standards of the International Steel Standard Committee on the Volumetric Determination of Phosphorus in Steel. Many years of work by five chemists of great experience in iron and steel analysis are represented in this report which is put forward tentatively to invite comment and criticism. The practice in the laboratories of iron and steel works in this country is undoubtedly the best in the world in respect to accuracy and rapidity, and it has been with these two ends in view that the committee has been working. Mr. Blair, as a member of this committee, has done a large amount of work both in determining the composition of the ammonium phospho-molybdate precipitate and also in devising useful modifications of the process and apparatus.

In an appendix there is a description of a rapid and accurate method of determining nickel and aluminum in steel by Mr. Chase of the Midvale Steel Works.

The third edition of this standard work will receive the same cordial welcome from chemists and teachers as its predecessors. It has become indispensable to all who work in the chemistry of iron.

THOMAS M. DROWN.

GAS AND FUEL ANALYSIS FOR ENGINEERS. A compend for those interested in the economical application of fuel. Prepared especially for the use of students at the Massachusetts Institute of Technology. By AUGUSTUS H. GILL, S.B., Ph.D. Assistant Professor of Gas Analysis. 89 pages. New York: John Wiley and Sons. 1896.

This book will be especially welcome to instructors in engineering schools since there is no other single small book covering the same ground. The topics considered are sampling, gas apparatus of Orsat, Bunte, and Elliott, measurement of temperature, calculation of air required to burn a fuel and loss of heat in flue gases, reagents, derivation, and composition of fuels, methods of analysis, and determination of heating value. Under the last head the Mahler bomb and Junker gas calorimeter are described and detailed directions given for their use.

The discussion of the topics is as satisfactory as could be expected in so small a book and but few mistakes have been noticed. There is, perhaps, too great a tendency to take data from various sources and insert them bodily without recalculation or verification and without putting the data in different parts of the book into forms which are consistent with each other.

The statement of the method of calculating the results of Berthier's test is not clear, and there should have been the further statement that the results obtained do not agree with the theory, and that the use of an empirical factor is necessary.

Instead of Lunge's formula for the calculation of the loss of heat in the flue gases, the following, which has been given by the writer to his students, gives a closer approximation and is simpler:

$$\text{Percentage loss} = \left(0.0111 + \frac{100 - \%\,CO_2}{\%\,CO_2}\,0.00605\right)(t' - t).$$

This formula is independent of the composition of the coal, in practical use.

W. A. N.

UNIVERSITY of ILLINOIS.

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ON THE DECOMPOSITION OF DIAZO COMPOUNDS.

IX.—ON THE REACTION OF ETHYL AND METHYL ALCOHOLS WITH PARADIAZOMETATOLUENESULPHONIC ACID IN THE PRESENCE OF VARIOUS SUBSTANCES.[1]

BY JOHN J. GRIFFIN.

Introduction.

Since it became known that the statement of Griess to the effect that, when diazo compounds are boiled with alcohol the decomposition products are nitrogen, aldehyde, and a substance formed by the replacement of the diazo group by hydrogen, does not hold good for all cases, but that in some cases the ethoxy group, and not hydrogen, enters into the compound, various efforts have been made to determine the conditions that decide which of these two reactions, known as the alkoxy and hydrogen reactions respectively, will take place. Work has been done in this laboratory on the influence of pressure and temperature on the reaction, and it has been shown that increase of pressure and simplicity of the alcohol radical favor the alkoxy reaction.

Metcalf,[2] in studying the reaction of certain alcohols with paradiazometatoluenesulphonic acid, showed that when the diazo compound is decomposed in alcohol, both the alkoxy and hydrogen reactions take place, the former greatly predominating, though the ratio changes somewhat with varying conditions of temperature and pressure. A few years later Beeson,[1] in his investigations on the action of certain diazo compounds on methyl and ethyl alcohols, carried on in this laboratory, having discovered the fact that the presence of an excess of alkalies and of some other substances induced the hydrogen reaction, it was thought desirable to study similar reactions in the case of paradiazometatoluenesulphonic acid.

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[1] From the Author's Thesis, submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1895. The work was undertaken at the suggestion of Professor Remsen, and carried on under his supervision.

[2] This JOURNAL, 15, 301.

Preparation of Paradiazometatoluenesulphonic Acid.

As a starting point the paratoluidinemetasulphonic acid of commerce was taken. This was a light brown powder, slightly soluble in cold, readily soluble in boiling water. After boiling with animal charcoal, two, or at most three, recrystallizations gave a pure white product, that separated from the solution in prismatic needles. By adding a little hydrochloric acid with the animal charcoal to the boiling solution the first crystallization gave a nearly white product.

Von Pechmann,[2] who obtained paratoluidinemetasulphonic acid by treating paratoluidine with fuming sulphuric acid, describes the product as of a sulphur yellow color which it was impossible to remove, and Metcalf,[3] who followed the same method of preparation, speaks of the difficulty of obtaining the acid in a pure white condition.

The pure white paradiazometatoluenesulphonic acid thus obtained was finely pulverized and diazotized by suspending it in alcohol of 92 per cent. and treating it with a strong current of nitrous fumes, produced by the action of nitric acid on arsenious oxide, in the manner described by Metcalf, and with substantially the same results.

100 grams of the acid were suspended in 30 cc. of alcohol, and the nitrous fumes passed through the emulsion for thirty minutes. The action was very slow at first, but soon increased as the mixture warmed up. The alcohol took on an orange color which deepened to a dark brownish red shade. The

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[1] This Journal, **16**, 235.

[2] Ann. Chem. (Liebig), **173**, 195.

[3] This Journal, **15**, 301.

diazo compound was of a light pink tint, and settled readily to the bottom of the flask after shaking, while, on the other hand, the alcohol with the suspended acid would remain milky for some time. This rapid settling to the bottom was taken as indicative of the completion of the reaction. The diazo compound was filtered off by means of a filter-pump, washed with a small quantity of alcohol and some ether and then dried. The yield in this and subsequent experiments, approached closely to the theoretical amount, never falling below 95 per cent. Some of the diazo compound dissolved in the alcohol and, on standing, crystallized out. The compound when dry keeps for months in the dark, but exposed to the light it slowly turns yellow. It is very stable, and small portions have been ground in a mortar without exploding.

Decomposition of Paradiazometatoluenesulphonic Acid in Methyl Alcohol in Presence of Various Substances.

1. *In Presence of Sodium Methylate.*—In 80 cc. of pure methyl alcohol, redistilled over lime, 5 grams of metallic sodium were dissolved. The solution of sodium methylate was then placed in a beaker in a freezing-mixture, and when its temperature fell below zero, the paradiazometatoluenesulphonic acid was added, small portions at a time. There was immediate action, a gentle evolution of gas took place, the diazo compound gradually disappeared, and the alcohol took on a straw yellow color. After the addition of a few small portions, the temperature rose to 5° and the color deepened. No further addition of the diazo compound was made until the thermometer had again fallen below zero, and the temperature was kept below that point throughout the experiment. When about half the diazo compound had been added, an orange-yellow powder began to settle in the bottom of the beaker. The addition of the diazo compound was continued until 25 grams had been added; the beaker was then removed from the freezing-mixture and left to stand over night. During the decomposition, a slightly irritating odor, other than that of the alcohol, could be observed. When the reaction had ceased the material was poured into an evaporating-dish, and the methyl alcohol driven off by heating on a water-bath.

The substance readily dried. When nearly dry, some volatile product, having a very irritating odor, and acting upon the eyes to produce an immediate flow of tears, began to be given off. The hard light-brown substance which remained in the dish was pulverized, and rubbed in a mortar, with its own weight (30 grams) of phosphorus pentachloride. The reaction was immediate and violent, and fumes of phosphorus oxychloride were given off. There remained behind a black viscid oil, together with a quantity of tarry products. This was poured into water, and a dark brown oil settled in the bottom of the vessel. Placed for some time in a test-tube, in a freezing-mixture, the oil did not solidify. The oil was washed with water several times and finally treated with strong ammonia, with which it readily reacted, going into solution and heating up considerably. Excess of ammonia was expelled by evaporating to dryness on a water-bath, and the residue extracted several times with ether. On distilling off the ether there remained behind a brown, syrupy liquid, which, on cooling, became solid and showed a crystalline structure. This was dissolved in boiling water and treated with animal charcoal and filtered. On cooling, small rhomboidal scales separated out, slightly brown in color. By several recrystallizations and treatment with animal charcoal, large clear white fern-shaped crystals were obtained which melted at 108°. This was the melting-point of the small quantity of metatoluenesulphonamide obtained by Metcalf from a mixture consisting for the greater part of paraethoxymetatoluenesulphonamide. The yield was 4.5 grams.

Another experiment was tried under similar conditions, with the exception of that of temperature, which was allowed to rise to 20°, and the results were essentially the same, with perhaps a slight increase in the tarry by-product. After the alcohol was evaporated off, a light brown color remained behind. This was heated on a water-bath until thoroughly dry. The same irritating odor was noticed. The alcohol which was distilled off was tested for aldehyde, and it responded at once to the silver-mirror test. A solution of the light brown powder was also tested for aldehyde, and its presence was indicated in the same way. By treatment with phosphorus pentachloride and ammonia, as in the first case, four grams of the amide were obtained. In these and the subsequent experiments, no product other than the metatoluenesulphonamide was obtained.

2. *In Presence of Sodium Carbonate.*—25 grams of the diazo acid were decomposed in 200 cc. of absolute methyl alcohol, in which 9 grams of dried sodium carbonate were suspended. When the alcohol had been cooled below zero, the addition of small portions of the diazo compound was begun. As the amount of substance added increased, the alcohol gradually took on a pink tinge, but, beyond an occasional bubble at long intervals, there was no apparent evolution of gas. The flask was then removed from the freezing-mixture, placed on a water-bath, and gently warmed to 30°, when a slow evolution of gas occurred. The flask was left standing over night. In the morning the alcohol was found to be colored brownish-red, and the sodium carbonate formed a layer at the bottom, seemingly in undiminished quantity. A thin layer of undecomposed or undissolved diazo compound covered the sodium carbonate. An occasional bubble of gas would rise through this upper layer. It was placed on a water-bath and heated to 35°, when the action became quite rapid, and continued till nearly all the sodium carbonate had disappeared. The temperature was then 46°. The flask was next connected with a condenser, and nearly all the alcohol was distilled off. The residual brown powder, dried on the water-bath, weighed 27 grams, and was darker in color than that obtained in the experiments with sodium methylate. By treating the salt in the usual way 12 grams of a light brown colored amide was obtained. A second experiment with sodium carbonate and methyl alcohol was performed, the alcohol being at the room temperature, 20°. A gentle evolution of gas began at once, and the temperature rose gradually while the diazo compound was added. It was not allowed to rise above 45°, being cooled when it reached that point by immersion in cold water. The remainder of the process was exactly as in the previous case, resulting in a like yield, 12 grams of amide.

3. *In Presence of Sodium Hydroxide.*—In this experiment, 7 grams of fused sodium hydroxide were broken up and placed

in an Erlenmeyer flask with 200 cc. of methyl alcohol. Small portions of the diazo compound were added, and the action was immediate, the temperature, which was 21° at the beginning of the experiment, rising so rapidly that the flask was placed in ice-water and kept there throughout the experiment. After 25 grams of the diazo compound had been added, the flask was left standing till all action had ceased, when the alcohol was distilled off as in the preceding cases. The yield of amide was 12 grams.

4. *In Presence of Zinc Dust.*—In a flask containing 200 cc. of absolute methyl alcohol, 10 grams of zinc dust were placed. The diazo compound was then added in small portions, the flask being well shaken after every addition. Action took place at once with a rapid rise of temperature from 17° at the beginning, to 30°. When this latter temperature was reached the flask was placed in ice-water. In this experiment the alcohol did not become discolored for a long time, whereas in the other decompositions, a very small proportion of the whole quantity of the diazo compound sufficed to give the alcohol a decided red color. When 25 grams of diazo acid had been added, the alcohol was of a light straw color.

After all action had ceased, the solution was filtered to remove the residual zinc dust. Five grams of pure white amide, melting at 108°, were obtained.

5. *In Presence of Calcium Carbonate.*—In this experiment 300 cc. of methyl alcohol and 15 grams of powdered calcium carbonate were taken. The diazo compound was added in small portions at a time, but no action was noticed. The flask was then placed on a water-bath, and heated up to 45°, but still there was no evolution of gas. Fifty grams of the diazo acid were added, and the whole left to stand over night. In the morning the calcium carbonate covered the bottom of the flask, with the lighter, undissolved diazo compound forming a layer above.

From this experiment it seems that the presence of calcium carbonate has no influence whatever on the diazo decomposition, which entirely agrees with Beeson's[1] results in his experiments with diazobenzene nitrate and calcite.

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[1] This Journal, **16**, 235.

An excess, 17 grams of zinc dust, was then added to the mixture. Bubbles of gas formed at once, and, as the contents of the flask became heated, the reaction went on briskly. The solution, which was of a pink color, soon became colorless, and at the conclusion of the action, it had the light yellow color observed in previous experiments with zinc dust. After filtering from the calcium carbonate and residual zinc dust, drying, and proceeding as before, a yield of 10 grams of pure white amide was obtained.

Decomposition of Paradiazometatoluenesulphonic Acid in Ethyl Alcohol in Presence of Various Substances.

1. *In Presence of Sodium Ethylate.*—3.5 grams of sodium were dissolved in 20 cc. of absolute ethyl alcohol, and the solution placed in a 500 cc. Erlenmeyer flask and cooled down to 5° below zero. The diazo compound was added in small portions at a time. Each portion sank at once to the botton of the flask, but in a few moments rose rapidly to the surface, colored dark red, and an evolution of gas began. The odor of aldehyde was very marked from the beginning. As the addition proceeded the solution thickened, and became very dark in color. The evolution of gas became sluggish and continued for a long time after all the diazo compound had been added. The temperature was kept below zero until 25 grams of the diazo compound had been added, when the flask was removed from the freezing-mixture, and the contents left to attain the room temperature.

The mixture was allowed to stand over night, then placed upon a water-bath, and the alcohol distilled off. A hard black mass remained in the flask. This could not be removed, and the alcohol was poured back into the flask and heated on the water-bath ; but the mass remained hard. It was left standing two and a half days, but with no better results. The alcohol was distilled off again, and the mass dissolved readily in a small quantity of water. This solution was evaporated to dryness over a water-bath. The dried mass was powdered and weighed 35 grams. It was of a dark brown color, much darker than the corresponding compound obtained from methyl alcohol. There remained a black viscous mass. This was shaken up with ether, the ether solution poured off, and the ether distilled off.

From this only 4 grams of dark-colored amide were obtained. The experiment was repeated with the same quantities of material, but no efforts were made to keep the temperature down. The only difference noted was in the rapidity of the reaction which, in the second experiment, was much greater than when the flask was kept in the freezing-mixture, but in neither case was it nearly as brisk as when methyl alcohol was employed. A yield of 3 grams of amide and a greater quantity of tarry matter than in the previous experiment, were obtained.

2. *In Presence of Sodium Carbonate.*—9 grams of dried sodium carbonate were suspended in 200 cc. of absolute alcohol, and, after cooling the mixture to zero, 25 grams of the diazo compound were gradually added. There was no apparent action. The flask was taken from the freezing-mixture and placed on a water-bath. When its temperature was 32° the action became brisk, but not nearly as much so as in the case of methyl alcohol and sodium carbonate. The odor of aldehyde was distinctly perceptible. The flask was kept on the water-bath till its contents attained a temperature of 50°. It was then removed, and left standing over night. In the morning the alcohol was colored a deep red, and bubbles of gas were still rising to the surface. Upon heating the flask the evolution of gas became very rapid. When this had almost entirely ceased the alcohol was distilled off. The brown mass remaining behind was removed very easily and powdered. It weighed 35 grams. From this 10 grams of pure white amide were obtained.

A second experiment was performed, the variation in this case consisting in using 90 per cent. alcohol in place of absolute alcohol. This experiment was performed at the room temperature. Upon the addition of the diazo compound there was a brisk evolution of gas, but no odor of aldehyde. The temperature of the contents of the flask rose up to above 40°. After standing a while it was heated on a water-bath to 45°, when the action proceeded briskly for some time, the sodium carbonate gradually disappearing, till but a small portion of it remained.

The odor of aldehyde was now perceptible. From this it seems that the reaction took place in two stages, the first being probably the formation of the sodium salt of paradiazometatoluenesulphonic acid, and the second the decomposition of this compound.

Proceeding as in the second experiment, 7 grams of a light brown amide were obtained.

3. *In Presence of Sodium Hydroxide.*—In this experiment an excess, 7 grams, of fused sodium hydroxide was broken up into small pieces and placed in an Erlenmeyer flask with 200 cc. of absolute ethyl alcohol. The experiment was begun at the room temperature. The reaction was similar to that with sodium ethylate, but the decomposition took place much more slowly than when methyl alcohol and sodium hydroxide were used. After distilling off the alcohol, drying and powdering, 35 grams of a brown substance were obtained. The yield of amide obtained was 10 grams, and its color was brown.

4. *In Presence of Zinc Dust.*—In this experiment 300 cc. of absolute ethyl alcohol and 17 grams of zinc dust were taken. 50 grams of the diazo compound were slowly added. No freezing-mixture was employed, but the temperature was kept down by placing the flask in running water.

The evolution of gas was a little sluggish at first, but, as the contents of the flask became warm, it became brisk. The odor of aldehyde was noticed from the very beginning. When the reaction was over the alcohol remained limpid and of a light orange color, in distinction to the dark-red, syrupy liquid which resulted from the other experiments with ethyl alcohol. The alcohol was distilled off, leaving a hard, almost white residue at the bottom of the flask. This gave 7 grams of a nearly pure white amide.

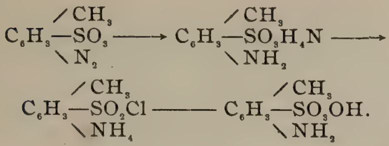
5. *In Presence of Ammonia.*—200 cc. of absolute methyl alcohol were saturated with dry ammonia gas and the solution was cooled to zero. Upon the addition of the diazo compound there was no apparent action. After waiting some time the flask was removed from the freezing-mixture and its contents were allowed to acquire the room temperature (20°), when action took place. As more diazo compound was added the temperature rose rapidly, and the flask was cooled

by placing it in a dish of cold water. Upon the completion of the reaction the alcohol was distilled off, the residue removed from the flask, dried and powdered. The powder was treated in a mortar with an equal amount of phosphorus pentachloride ; the reaction was very violent ; fumes of phosphorus oxychloride were given off, but in place of the appearance of an oil, the mixture in the mortar thickened and became solid. Water was added to this, upon which the mass foamed up, and after the reaction was over bunches of yellow needles appeared throughout the dark red liquid.

A quantity of crystals was removed and washed with water. They were found to be very soluble in water. Repeated boiling with animal charcoal failed to remove or lessen their yellow color. Heated up to 300°, they charred without melting. On adding hydrochloric acid to a solution of the substance, white needles, similar in appearance to the original paratoluidinemetasulphonic acid, crystallized out. It was supposed that it might be the ammonium salt of paratoluidinemetasulphonic acid, and to test this about 20 grams of it was diazotized in the usual manner, and the diazo compound, similar in appearance to that obtained heretofore, was then decomposed in absolute methyl alcohol, to which an excess of fused sodium hydroxide had been added. The decomposition took place in all respects similar to that of the diazo acid in methyl alcohol and sodium hydroxide. On drying, powdering, and treating with phosphorus pentachloride, a dark-colored oil was obtained, which was washed and treated with ammonia. The resulting amide was extracted with ether, boiled with water and animal charcoal, and brown crystals were obtained which, by repeated purifications, gave large pure white scales, of exactly the same appearance as the recrystallized amides previously obtained, and melting at the same temperature.

The experiment was repeated, using ethyl alcohol, with like results.

Hence the decomposition of paradiazometatoluenesulphonic acid in ammoniacal alcohol, must have taken place as follows :



$$C_6H_3{-}\begin{array}{l}/\,CH_3\\ SO_3\\ \backslash\,N_2\end{array} \longrightarrow C_6H_3{-}\begin{array}{l}/\,CH_3\\ SO_3H_4N\\ \backslash\,NH_2\end{array} \longrightarrow$$

$$C_6H_3{-}\begin{array}{l}/\,CH_3\\ SO_2Cl\\ \backslash\,NH_4\end{array} \text{———} C_6H_3{-}\begin{array}{l}/\,CH_3\\ SO_3OH.\\ \backslash\,NH_2\end{array}$$

A comparison of the different yields of purified amides was made as follows, the number representing the yield in grams of pure amide obtained from the decomposition of 100 grams of the paradiazometatoluenesulphonic acid.

	In methyl alcohol.	In ethyl alcohol.
With sodium...........	24.8	19.0
‘‘ sodium carbonate..	36.0	33.0
‘‘ sodium hydroxide.	33.0	24.0
‘‘ zinc dust.........	17.0	24.0

Each weight is the average of at least three experiments.

From these experiments it is seen that the sodium carbonate reaction yielded the largest amount of amide. The compound resulting from the decomposition of the diazo acid in presence of sodium carbonate, and which contained the excess of sodium carbonate originally added, was also the one most slowly acted upon by phosphorus pentachloride.

On the other hand, with the exception of the zinc dust reaction, all the others gave a quantity of tarry matter upon treatment with phosphorus pentachloride.

The apparent purity of the oil obtained by treating with phosphorus pentachloride the product of the decomposition of paradiazometatoluenesulphonic acid in the presence of zinc dust; the absence of all traces of tarry matter; and the large clear white crystals of amide which the very first crystallization yielded, marked the zinc reaction as by far the cleanest method of decomposition. The great disparity in the yields of amide obtained by this and the other methods of decomposition, was not, however, in its favor.

It was thought that the heat of the reaction might have decomposed or volatilized a part of the sulphonchloride formed, and experiments were made with a less violent chlorinating agent than phosphorus pentachloride. Accordingly 50 grams of the diazo compound were decomposed in 300 cc. of methyl alcohol and 17 grams of zinc dust. After the decomposition, the solution was filtered and evaporated to dryness, 55 grams of a light-brown powder being obtained. This was added in small portions at a time, to 70 grams of phosphorus trichloride, contained in a 300 cc. round-bottomed flask. After a few grams had been added small bubbles began to appear, coming from the powder, which darkened somewhat in color, and became gummy. As the addition of substance went on, the temperature rose very slightly. After the whole had been added the flask was put aside over night.

In the morning the contents of the flask consisted of a brown gum, which covered the bottom, and an almost clear liquid on top. Most of the clear liquid, the greater part of which was phosphorus trichloride, was poured off, placed in a flask, and distilled under diminished pressure. There remained behind a small quantity of a slightly yellow oil. This was shaken up with water; it became lighter in color, diminished somewhat in quantity, and settled readily to the bottom of the flask.

The flask containing the gummy substance and the remainder of the clear liquid, was then connected with a condenser, and heated on a water-bath under diminished pressure. Some more phosphorus trichloride came over. When distillation had ceased the flask was removed, and the slightly yellow liquid above the gummy material poured into water. It settled at once to the bottom. Water was added to the flask containing the brown gum, and this dissolved slowly, giving off small globules of oil which gathered together at the bottom. The three portions of oil were put together and washed repeatedly with water.

The amide was made by pouring the oil into 150 to 200 cc. of strong ammonia, and shaking vigorously. In a few minutes the contents of the flask became warm and the oil dissolved, forming a clear, light-yellow solution. Upon cooling, large, slightly yellow crystals of the amide separated out. After filtering, the mother-liquid was evaporated to dryness and the residue extracted with ether, which resulted in a still smaller addition to the total amount of amide obtained. After boiling with animal charcoal, the first crystallization yielded, from 100 grams of the diazo compound, 45 grams of large pure white fern-shaped crystals, which melted sharply at 108°.

The decomposition was repeated, using absolute ethyl alcohol in place of methyl alcohol. The decomposition did not take place as readily as when methyl alcohol was employed, but, upon slightly warming the alcohol, it became rapid. The alcohol remained nearly colorless throughout the experiment, while when methyl alcohol was used, it turned to an orange color. The yield of amide was a little greater than by the methyl alcohol method, 100 grams of the diazo acid giving 50 grams of pure amide.

The results obtained by heating the product of the diazo decomposition in presence of zinc dust with phosphorus trichloride, suggested a like experiment with that obtained by decomposing the diazo acid in presence of sodium carbonate.

Because the amides obtained by treating the residue, after the decomposition in presence of sodium carbonate, with phosphorus pentachloride and ammonia respectively approached that from the zinc dust reaction in whiteness and surpassed it in quantity, it was thought the substitution of the trichloride for the pentachloride of phosphorus, would lead to a larger and cleaner yield of metatoluenesulphonchloride.

Accordingly, about 25 grams of the diazo compound were decomposed in absolute ethyl alcohol in which 8 grams of dried sodium carbonate were suspended.

The reaction took place as in the like experiments previously performed, and about 30 grams of dried material were obtained. This was powdered, and added little by little, to 30 grams of phosphorus trichloride. Each small portion added settled to the bottom, and there was no appearance of change. When the whole amount was added, the powder absorbed the liquid trichloride, but the contents of the flask did not warm up, nor was any other indication of a reaction noticed. Left to stand over night, its appearance was unchanged in the morning.

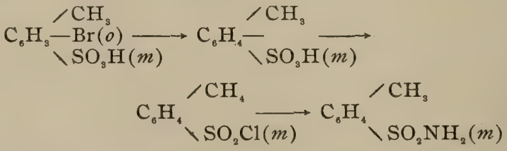
The flask was next connected with a reflux-condenser, and heated on a water-bath for two hours. A portion of the moist powder was then recovered from the flask and thrown into cold water. There was the usual reaction between phosphorus trichloride and water, but no trace of an oily sulphonchloride. The substance was therefore removed from the flask and rubbed in a mortar with 30 grams of phosphorus pentachloride, resulting in the usual quantity of liquid metatoluenesulphonchloride, which was converted into the amide.

From this experiment it was concluded that the product obtained when the diazo compound was decomposed in presence of sodium carbonate would not react with phosphorus trichloride and all subsequent yields of sulphonchloride were obtained by the zinc dust and phosphorus trichloride treatment.

Metatoluenesulphonamide.

Having on hand a quantity of pure amide, obtained as a result of the preceding experiments, its properties were carefully studied and compared with the metatoluenesulphonamides described in the literature.

The amide was first mentioned, in 1873, by Müller,[1] who made it by reducing the barium salt of orthobrommetatoluenesulphonic acid, by means of sodium amalgam, and then by the phosphorus pentachloride reaction forming the sulphonchloride, which, treated with ammonia, gave the amide. The transition from the orthobrommetatoluenesulphonic acid to the amide, he supposed took place as follows:



$$C_6H_3\begin{array}{l}\diagup CH_3\\ -Br(o)\\ \diagdown SO_3H(m)\end{array} \longrightarrow C_6H_4\begin{array}{l}\diagup CH_3\\ -\\ \diagdown SO_3H(m)\end{array} \longrightarrow$$

$$C_6H_4\begin{array}{l}\diagup CH_4\\ \\ \diagdown SO_2Cl(m)\end{array} \longrightarrow C_6H_4\begin{array}{l}\diagup CH_3\\ \\ \diagdown SO_2NH_2(m)\end{array}$$

Müller describes the amide as easily soluble in ether, alcohol and ammonia, and as crystallizing from water at 40° in large scales, and from water at 20° in slender needles. Its melting-point was 90°–91°.

A year later Pechmann[2] obtained what he claimed to be metatoluenesulphonamide by decomposing paradiazometatoluenesulphonic acid in alcohol under pressure, according to the following equation:

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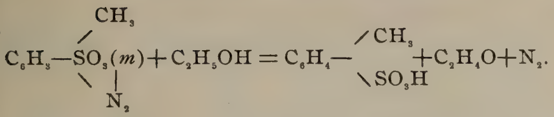
[1] Ann. Chem. (Liebig), **169**, 51.

[2] *Ibid.* **173**, 195.



$$C_6H_3{-}\overset{\overset{CH_3}{\diagup}}{\underset{\underset{N_2}{\diagdown\;|}}{SO_3}}(m)+C_2H_5OH=C_6H_4{-}\begin{matrix}\diagup CH_3\\ \diagdown SO_3H\end{matrix}+C_2H_4O+N_2.$$

From this acid he obtained an amide, like Müller's, soluble in hot water, alcohol and ether, but which crystallized in rhombic scales and in brilliant leaves and needles, and melted "somewhere below 100°."

The amide was next obtained in 1874, by Pagel,[1] who also employed the diazo reaction, making first the diazo compound of orthotoluidinesulphonic acid, changing this into the bromtoluenesulphonic acid, removing the bromine by long-continued treatment with sodium amalgam, and then proceeding to the amide by the usual reactions. Pagel's amide was tolerably easily soluble in cold water, much more so in hot water, and easily soluble in alcohol, chloroform, and ether. From all these solvents it crystallized out in large leaves, which melted at 104°.

In 1877, Beckurts[2] described an amide which he obtained by fractional crystallization from a mixture of amides. But this product, and that obtained two years later by Claesson and Wallin,[3] was a mixture of the para and ortho compounds, as will be shown in the second part of this thesis.

In 1879, F. H. S. Müller,[4] by treating the metadiazotoluene salts with sulphurous acid, obtained an amide melting at 107°. This also was probably impure, for an anilide obtained from the same sulphonchloride, had a much lower melting-point than the one which will be described further on.

Neville and Winther,[5] (1880), by heating orthodiazotoluenesulphonic acid under pressure with alcohol, and by reduction of bromtoluenesulphonic acid by means of sodium amalgam, obtained a toluenesulphonic acid, which gave, on treating its potassium salt with phosphorus pentachloride, a sulphonchloride, and an amide which melted at 106°.5–107°.5.

Chase Palmer,[6] in 1882, repeated Hübner and Müller's process of obtaining the amide, and found a product identical in all its properties with that described by these investigators.

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[1] Ann. Chem. (Liebig), **176**, 297.

[2] Ber. d. chem. Ges., **10**, 943.

[3] *Ibid*, **12**, 1848.

[4] *Ibid*, **12**, 1348.

[5] J. Chem. Soc., **37**, 628.

[6] This Journal, **4**, 140.

In 1886, Klason[1] prepared the amide after the method of Pechmann, and found it to have a melting-point of 108° crystallizing in monoclinic scales and octahedra.

In the same year Vallin,[2] admitting the evidence of the impurity of the amide obtained by himself and Klason,[3] made the compound by the method of Pechmann and described it as crystallizing from water in leaves melting at 107°, and from alcohol in monoclinic crystals which melted at 108°. About this time also, Noyes and Walker[4] made what they claimed to be the metatoluenesulphonamide by treating orthobromtoluene with fuming sulphuric acid, making the sodium salt and eliminating the bromine atom by means of zinc dust. The sodium salt was then treated with phosphorus pentachloride and the oily chloride thus obtained converted into an amide which melted at 90°–91°.

The next contribution to our knowledge of metatoluenesulphonamide was made by Metcalf,[5] in his work "On the Reaction of Certain Alcohols with Paradiazometatoluenesulphonic Acid," which showed that when this acid is decomposed by boiling with alcohol, both the alkoxy and the hydrogen reactions take place, the former to a much greater degree than the latter. Metcalf succeeded in separating a small quantity of the metatoluenesulphonamide from mixtures of it and paraethoxymetatoluenesulphonamide. He found for these specimens melting-points ranging between 95° and 108°.

The amide which was obtained in the experiments herein described was carefully compared with that described by the above-mentioned investigators.

The specimens resulting from the phosphorus pentachloride reaction were boiled with animal charcoal and recrystallized six times. That which resulted from the sulphonchloride obtained by the phosphorus trichloride treatment, gave pure white crystals after its first recrystallization. From concentrated solutions the amide came down in brilliant hexagonal scales, and from more dilute solutians it separated out in beautiful large fern-like growths. It is soluble to a very slight extent in cold water, but easily soluble in hot water at a temperature of 70°. It is exceedingly soluble in alcohol, from which it crystallizes in large monoclinic prisms.

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[1] Ber. d. chem. Ges., **19**, 2887.

[2] *Ibid.*, **19**, 2952.

[3] *Ibid*, **12**, 1848. The names of these two investigators were written Clæsson and Wallin.

[4] This JOURNAL, **8**, 186.

[5] *Ibid.*, **15**, 301.

Analyses of the amide gave the following results:

I. 0.3020 gram of the amide gave 0.5445 gram of carbon dioxide, and 0.1472 gram water.

II. 0.3003 gram of the amide gave 0.5425 gram of carbon dioxide, and 0.1450 gram water.

III. 0.2391 gram of the amide gave 0.3302 gram of barium sulphate.

IV. 0.2910 gram of the amide gave 0.3950 gram of barium sulphate.

V. 0.2210 gram of the amide gave 0.0202 gram of nitrogen.

VI. 0.1800 gram of the amide gave 0.0149 gram of nitrogen.

VII. 0.2185 gram of the amide gave 0.0178 gram of nitrogen.

The sulphur determinations were made by Liebig's method. Nitrogen determination V. was made by the Dumas method; VI. and VII. were made, by Wilfarth's modification of the Kjeldahl method, by Mr. J. W. Lawson, of this laboratory, who also made the carbon and hydrogen determinations.

	Calculated for $C_6H_4<\begin{smallmatrix}CH_3\\SO_2NH_2\end{smallmatrix}$.	Found. I.	 II.
C	49.12	49.17	49.26
H	5.26	5.40	5.36
S	18.71	18.92	18.73
N	8.18	8.15	8.28–8.15

The amide obtained by Müller[1] was described as crystallizing at 20° in slender needles. Though a great many observations were made, in no case did the amide come down in this form, but always in hexagonal scales sometimes bunched in fern-shaped leaves.

Von Pechmann's amide came down in rhombic scales and needles, and though it melted at 104°, was far from being

[1] Ann. Chem. (Liebig), **169**, 51.

pure metatoluenesulphonamide, for, as shown by Metcalf's work, it contained some paraethoxymetatoluenesulphonamide. Pagel's amide differed from that herein described in being tolerably easily soluble in cold water and in crystallizing from all its solvents in large leaves. The other amides referred to above, which were prepared after the methods of Müller and von Pechmann, or a combination of both, cannot be considered as pure products.

Oxidation of Metatoluenesulphonamide.

An experiment was made, having for its aim the oxidation of metatoluenesulphomamide to metasulphaminebenzoic acid. To a mixture of 80 grams of concentrated sulphuric acid diluted with three times its volume of water, and 60 grams of potassium bichromate, 20 grams of metatoluenesulphonamide were added. The flask containing the mixture was connected with a reflux-condenser and heated gently over a low flame. The action began almost immediately, and became so energetic that cold water had to be added to the contents to prevent foaming over. After boiling for an hour, the oily layer of melted amide which covered the surface entirely disappeared, and the flask was removed and its contents, after cooling, were poured in cold water. A mass of crystals separated. These were filtered by means of a filter-pump, and washed with water till free from color. They were then treated on the funnel with cold sodium carbonate solution, when most of the acid dissolved. The substance which remained on the filter was examined and proved to be pure metatoluenesulphonamide. It weighed about two grams.

Metasulphaminebenzoic Acid.

The sodium salt, which passed in solution through the filter, was treated with hydrochloric acid and a quantity of minute scales separated out. These were filtered off, dried, and recrystallized. They gave a melting-point of 233° (uncorrected). From the 20 grams of metatoluenesulphonamide a yield of 12 grams of the metasulphaminebenzoic acid resulted. It was carefully compared with the metasulphaminebenzoic acid which Limpricht and Uslar[1] obtained by heating together sulphobenzamide and potassium hydroxide, and which was described as separating from cooled mixture in scales melting above 200°. This acid was further described as sparingly soluble in cold water, more easily in ether, and very soluble in alcohol. Kept in a molten state for ten minutes, it stiffened on cooling to a crystalline mass easily soluble in water. Its barium salt was made by adding barium carbonate to a boiling solution of the acid. This was easily soluble in water, from which it crystallized out in small masses resembling wavellite, and containing four molecules of water of crystallization. Its silver salt consisted of long silky needles which contained two molecules of water of crystallization and did not blacken on boiling or long exposure to the light.

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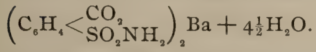
[1] Ann. Chem. (Liebig), **106**, 36.

A small portion of the metasulphaminebenzoic acid, made by oxidizing metatoluenesulphonamide, was gently heated upon platinum foil. It behaved like Limpricht and Uslar's acid, volatilizing, and passing off in white fumes free from the irritating effect of the fumes of benzoic acid. About one gram of the acid was heated in a test-tube in a sulphuric-acid bath to 245°–250° for forty-five minutes. Upon cooling, it stiffened to a brown, glassy mass, which was easily soluble in cold water, from which it crystallized out, on evaporating down the solution, in long needles.

Barium Salt of Metasulphaminebenzoic Acid.—The barium salt of the acid was made by neutralizing a boiling solution of the acid by means of pure barium carbonate. The undecomposed carbonate was filtered off and the solution evaporated down. Upon standing, small radiating nodules formed like those described by Limprict and Uslar.

The analysis of the barium salt showed its composition to be



$$\left(C_6H_4<\begin{matrix}CO_2\\SO_2NH_2\end{matrix}\right)_2Ba + 4\tfrac{1}{2}H_2O.$$

I. 0.2345 gram of the barium salt, dried by exposure to the air, lost, upon being heated to 180°, 0.0306 gram water.

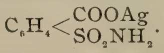
II. 0.3022 gram of the salt, gave off at 180°, 0.0394 gram water.

III. 0.2039 gram of the anhydrous barium salt, gave upon ignition with sulphuric acid, 0.0880 gram of barium sulphate.

IV. 0.2623 gram of the anhydrous salt, gave 0.1126 gram of barium sulphate.

	Calculated.	Found.	
		I.	II.
H_2O	13.10	13.05	13.03
Ba	25.51	25.37	25.24

The dehydrated salt takes up water very rapidly, which makes its weighing difficult. The difference between our results for the water of crystallization and those of Limpricht and Uslar, may be due to this, and also to the fact that their barium salt was dried over sulphuric acid, and was heated only to 110°.

Silver Salt—The silver salt was made by boiling a solution of the acid with silver carbonate. It was soluble to a slight extent in boiling, and insoluble in cold water. From hot water it crystallized out in long, fine needles, which slowly blackened upon exposure to the light. It contained no water of crystallization, and analysis showed that it corresponded to the formula  $C_6H_4<\begin{matrix}COOAg\\SO_2NH_2\end{matrix}$.

I. 0.2256 gram of the salt gave 0.0779 gram silver.

II. 0.2710 gram of the salt gave 0.0945 gram silver.

	Calculated.	Found.	
		I.	II.
Ag	35.06	35.52	34.90

Limpricht and Uslar found two molecules of water of crystallization in this salt.

On the whole, if we except the water of crystallization of the silver salt, there are enough points of resemblance between the salts of metasulphaminebenzoic acid obtained by the oxidation of metatoluenesulphonamide, and those of Limpricht and Uslar's compound, to indicate the identity of the two substances.

Conclusions.

From the work described in this article we may conclude that:

1. When paradiazometatoluenesulphonic acid is decomposed in alcohol in the presence of an excess of some alkalies and zinc dust, only the hydrogen reaction takes place.

2. When the decomposition takes place in alcohol saturated with ammonia, the ammonium salt of paratoluidinemetasulphonic acid is formed.

3. The nature of the alcohol, whether methyl or ethyl alcohol, has little, if any, influence on the reaction.

4. If we except the case of decomposition in the presence of calcium carbonate, countenance is given to the suggestion that the neutralization of free acid determines the hydrogen reaction. But why calcium carbonate acts differently has not yet been determined.

ON METATOLUENESULPHONIC ACID.

By John J. Griffin.

Introduction.

The action of sulphuric acid on toluene was first investigated by Jaworsky,[1] who described one toluenesulphonic acid as the resulting compound.

In 1869, Engelhardt and Latschinoff[2] heated toluene with sulphuric acid, and made the potassium salt of the resulting acid. This crystallized out in two forms: prisms which were difficultly soluble, and needles which were more easily soluble in water. These two potassium salts were fused with caustic potash and gave two isomeric cresoles, the para and ortho compounds.

Barth,[3] working in a similar manner, obtained, by fusing the crude mixture of potassium salts, paroxybenzoic and salicylic acids.

Anna Wolkow[4] confirms this result, but ascribes the meta position to the sulphon group in the acid which passed over into salicylic acid, and further, made two sulphonchlorides, one liquid and one solid, and two amides, that from the α or para acid melting at 137°, and that from the β or, as it was then called, the meta acid, melting at 153°–154°.[5]

Fittig and Ramsay,[6] in order to settle definitely the position of the sulphon group in the acid which Anna Wolkow called the metatoluenesulphonic acid, proceeded as follows: They treated toluene with sulphuric acid, made the isomeric potassium salts, and separated as far as possible by fractional crystallization, the para salt. The mother liquid, which contained some of the para and an isomeric salt which was either ortho or meta, was then evaporated to dryness and thoroughly mixed with potassium cyanide. This mixture was distilled in an iron retort; the oily liquid which came over was heated with caustic potash till free from ammonia. After washing with ether, the potassium salt was acidified and the toluic acid extracted with ether. This was a mixture of paratoluic with either ortho- or metatoluic acid. An easy method of separation was found by treating the calcium salts with alcohol, in which the para salt was not soluble. By this means they obtained, not the meta, but the orthotoluic acid. They further confirmed their work by oxidizing this orthotoluic acid by means of a mixture of potassium bichromate and dilute sulphuric acid, and obtained as a product neither isophthalic nor terephthalic acid, which showed conclusively, that the isomeric acid formed together with paratoluenesulphonic acid when toluene is treated with sulphuric acid, is not the meta, but the para, compound.

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[1] Ztschr. Chem., **1**, 272.

[2] *Ibid*, (1869), 617.

[3] Ann. Chem. (Liebig), **152**, 91.

[4] Ztschr. Chem. (1870), 321.

[5] This was previous to V. Meyer's work on the orientation of the hydroxybenzoic acids.

[6] Ann. Chem. (Liebig), **168**, 242.

The next contribution to our knowledge of the isomeric toluenesulphonic acids, was a consequence of the work of Hübner and Post[1] on bromotoluene and the behavior of its hydrogen atoms.

By the action of sulphuric acid on crystallized bromotoluene, which they showed to be a para compound, two isomeric bromotoluenesulphonic acids were obtained, which they designated as the α- and β-parabromotoluenesulphonic acids. The β-acid was treated with sodium amalgam in order to remove the bromine atom, and the toluenesulphonic acid thus obtained, was fused with potassium hydroxide. Salicylic acid was obtained, which was evidence that the sulphon group was in the position ortho to the methyl group. It was, therefore, by exclusion, concluded that the α-acid must have the sulphon group in the meta position.

F. C. G. Müller[2] made the barium salt of orthobromtoluene-sulphonic acid and treated it, in solution, with sodium amalgam, in order to remove the bromine atom from its molecule. The excess of alkali was neutralized with sulphuric acid, the sodium sulphate removed by evaporation and crystallization, and the residue dried. The dried mass was treated with phosphorus pentachloride, and an oily toluenesulphonchloride was obtained. This was heated with water to 130°, and the resulting acid mixture was freed from hydrochloric acid by evaporation and the passage of a current of air through it. The toluenesulphonic acid was obtained as a syrup, which stiffened to a crystalline condition. Various salts of the acid were made, some of which will be described later on. The amide obtained melted at 90°–91°. Because this toluenesulphonic acid differed from both the ortho and para acids, Müller considered it to be metatoluenesulphonic acid.

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[1] Ann. Chem. (Liebig), **169**, 47.

[2] *Ibid*, **169**, 47.

About the same time F. Gerver[1] made orthodiazotoluenesulphonic acid by subjecting orthotoluidinesulphonic acid to the action of nitrous fumes. The diazo compound was decomposed in alcohol under pressure. The sodium salt of the sulphonic acid obtained was made, and gave upon treatment with phosphorus pentachloride, a fluid sulphonchloride, which was converted by the action of ammonia into an amide melting at 148°, and differing in this and other properties, from the ortho and para amides previously known.

In 1874 Pechmann[2] obtained a quantity of paratoluidinemetasulphonic acid by heating sulphuric acid with paratoluidine, and crystallizing out the paratoluidineorthosulphonic and the disulphonic acids formed, leaving the paratoluidinemetasulphonic acid, on account of its greater solubility, in solution.

From this solution the paratoluidinemetasulphonic acid crystallized out in sulphur-yellow needles which could not be decolorized by repeated boiling with animal charcoal. By precipitation from its salts, however, it was obtained colorless. It was difficultly soluble in cold water, one part of acid requiring ten parts of water for its solution.

The diazo compound was made by suspending the finely divided acid in alcohol, and treating it with nitrous fumes.

[1] Ann. Chem. (Liebig), **169**, 383.

[2] *Ibid*, **173**, 195.

This was then decomposed by heating it under pressure with alcohol.

Various salts of the resulting sulphonic acid were made which showed some differences from those of Müller, also an amide which melted somewhat below 100°.

In 1875, Pagel,[1] working on orthotoluidinesulphonic acid, obtained a toluenesulphonic acid which resembled Müller's meta acid.

A mixture of alcohol and sulphuric acid was neutralized with lime, and the resulting calcium ethyl sulphate was decomposed by the addition of a solution of the orthotoluidine salt of oxalic acid. By filtration and crystallization, crystals of orthotoluidine ethyl sulphate were obtained, which were decomposed into alcohol and orthotoluidinesulphonic acid by being heated to 180°–200° in an air-bath.

The orthotoluidinesulphonic acid was changed into the diazo compound, and this transformed into bromotoluenesulphonic acid.

By proceeding as Müller did, a toluenesulphonic acid was obtained which agreed tolerably well with Müller's metatoluenesulphonic acid, if we except the melting-point of the amide, which Pagel found to be 104°.

In 1877, H. Beckurts,[2] seeking for a method by which to obtain a good yield of pure orthotoluenesulphonic acid, heated a mixture of ordinary sulphuric acid and toluene and made the potassium salts of the resulting sulphonic acids in the usual manner. By treatment with phosphorus pentachloride a mixture of sulphonchlorides was obtained, from which the paratoluenesulphonchloride crystallized out upon cooling the mixture to 15° below zero.

The remaining liquid sulphonchloride was transformed into the amide compound, which was purified and subjected to fractional crystallization. Two compounds were obtained, one difficultly soluble in alcohol, which melted at 153°–154°, the other easily soluble in the same medium, and melting at 104°. From this work, Beckurts concluded that the action of sulphuric acid on toluene, resulted in the formation of the three isomeric sulphonic acids. The work was pursued further, and some of the amide heated with hydrochloric acid in a sealed tube to 150°. The ammonium salt of the acid was thus obtained, and from a portion of this, treated with barium hydroxide, the barium salt. From a comparison of these salts with the ammonium and barium salts obtained by Müller, Beckurts asserts that they were salts of metatoluenesulphonic acid.

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[1] Ann. Chem. (Liebig), **176**, 297.

[2] Ber. d. chem. Ges., **10**, 943.

Fahlberg,[1] working in this laboratory, doubted the statement that Beckurts had obtained metatoluenesulphonic acid, because, though his product showed differences from the ortho and para compounds, he neglected to prove its constitution by converting it into an oxybenzoic acid. Fahlberg repeated Beckurts' work, with the sole exception that water, and not alcohol, was used as the medium for fractional crystallization.

The liquid sulphonchloride, from which no more solid parasulphonchloride separated out when cooled to 15° below zero, was treated with aqueous ammonia. As products there were obtained α-toluenedisulphonamide, melting at 186°–187°, and a yellow mixture of amides. This latter he subjected to fractional solution; whereby only a portion dissolved. The undissolved amide melted at 153°–154°, and gave upon fusing with caustic potash, salicylic acid. Therefore it was orthotoluenesulphonamide. From the soluble portion of the mixture, two compounds were obtained by fractional crystallization. That less soluble, on purification, proved also to be orthotoluenesulphonamide.

From the solution of the more soluble portion an amide crystallized out, which melted at 120°, but repeated purifications from animal charcoal lowered the melting-point to 108°, where it remained constant. A quantity of the amide which melted at 108° was oxidized by means of potassium permanganate, and three products were obtained; parasulphaminebenzoic acid, anhydroorthosulphaminebenzoic acid, and acid potassium orthosulphobenzoate; which were the products one would expect to result from the oxidation of a mixture of para and orthotoluenesulphonamides.

Further evidence that Beckurts' amide, despite the constancy of its melting-point, was a mixture, was given by the following experiment: Equal parts of pure para- and orthotoluenesulphonamides were dissolved in water and the mixture subjected to recrystallization. Two forms of crystals were obtained: long fine needles which melted constantly at 120° and leaves which fused at 108°. Slight impurities lowered the melting-point to 104°–105°, as in the case of Beckurt's amide. F. H. S. Müller,[1] in 1879, mentioned the formation of metatoluenesulphonic acid by the action of sulphurous acid on the corresponding diazo compounds; but beyond the melting-points of the amide, anilide and toluidide, gave no details of his work.

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[1] This JOURNAL, **1**, 179; Ber. d. chem. Ges., **10**, 1048.

Claesson and Wallin,[2] in 1879, claimed that they had obtained metatoluenesulphonic acid by the action of chlorsulphonic acid on toluene. These investigators worked with large quantities of material, bringing together in small portions at a time, 2800 grams of chlorsulphonic acid and 1119 grams of toluene.

The solid parasulphonchloride was removed by cooling the mixture, and the liquid chlorides converted into the amides. Two amides were separated by fractional crystallization, the ortho compound melting at 153°–154°, and the other, supposed to be the meta, melting constantly at 107°–108°. This latter was transformed into the toluenesulphonic acid by being heated with water in a sealed tube to 150°. and various salts were made. These were compared with the salts made by Müller, and also with the analogous salts of the para and ortho acids. From this, despite the fact that they had knowledge of Fahlberg's work, Claesson and Wallin concluded that all three isomeric acids were formed as a result of the action of sulphuric acid on toluene.

The next step in the controversy was taken by R. Otto,[3] who, at the request of Beckurts, examined carefully the specimen of so-called metatoluenesulphonamide, which the latter had obtained three years previously, and which was claimed by Fahlberg to be a mixture, and by Claesson and Wallin, to be metatoluenesulphonamide. The substance, weighing about 10 grams, was heated with hydrochloric acid in a sealed tube. The sulphonic acid formed was converted into the potassium

[1] Ber. d. chem. Ges., **12**, 1348. [2] *Ibid*, **12**, 1848. [3] *Ibid*, **13**, 1292.

salt, and this was treated with phosphorus pentachloride, with the formation of an oil which soon stiffened and the solid portion of which was freed from the fluid by pressure. This latter portion was dissolved in benzene, from which it crystallized out in large scales which had the same melting-point as paratoluenesulphonchloride, and gave a corresponding amide and anilide. This was conclusive evidence that metatoluenesulphonic acid was not obtained by Beckurts.

Neville and Winther,[1] in 1880, investigated the formation of amidosulphonic acids by the action of concentrated sulphuric acid, obtained a toluenesulphonic acid by heating orthodiazotoluenesulphonic acid under pressure with alcohol, and by reducing bromotolueneorthosulphonic acid by means of sodium amalgam. By treating the potassium salt with phosphorus pentachloride they obtained a liquid sulphonchloride which gave, in both cases, an amide melting at 106°.5–107°.5, whence they concluded that the acid which they had obtained was metatoluenesulphonic acid.

In 1886, Valin,[2] convinced by the work of Otto, that Fahlberg's views were correct, and that he and Klason had not obtained metatoluenesulphonic acid, again attacked the problem of obtaining the compound. Pechmann's method was followed; an acid was obtained, and a series of salts made and described.

The work of Metcalf[3] furnished evidence that the decomposition of paradiazometatoluenesulphonic acid by boiling with alcohol under pressure, resulted in the formation of paraethoxymetatoluenesulphonic acid in far greater proportion than metatoluenesulphonic acid. Consequently, neither by Pechmann nor by Valin had the acid been obtained.

Preparation of Metatoluenesulphonic Acid.

In consideration of all this dissentient testimony in regard to metatoluenesulphonic acid and of the fact that pure metatoluenesulphonamide is now by my researches made available in any desired quantity, it was thought desirable to transform the amide into the acid and study its properties. Sealed tubes containing 25 grams of the pure amide and a quantity of hydrochloric acid were heated to 140° for six hours. Upon cooling the tubes contained a mass of clear white fern-shaped crystals entirely different in form from the crystals of the amide. These proved to consist entirely of ammonium chloride.

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[1] J. Chem. Soc., **37**, 628.

[2] Ber. d. chem. Ges., **19**, 2952.

[3] This JOURNAL, **15**, 301.

The fluid portion of the contents of the tube was evaporated down on a water-bath, water added and evaporated, and this process repeated until the greater portion of the hydrochloric acid was removed. The solution was then boiled with potassium hydroxide solution until no further evolution of ammonia was evident. The solution, which contained the potassium salt of metatoluenesulphonic acid and some potassium chloride, was then evaparated down until it solidified in a mass of scales. These were powdered and boiled with alcohol of 95 per cent. The greater portion of the salt dissolved, and separated out on cooling, in a mass of minute scales which nearly filled the beaker. From the mother-liquor more of the salt was obtained by evaporation. The undissolved portion was subjected to several more extractions until potassium metatoluenesulphonate no longer crystallized out of the solution. The residue was then examined and found to be potassium chloride. The crystals from the alcoholic solution were collected on a filter and dried. They were then powdered and heated in an air-bath for an hour to 160°. Upon cooling, the substance was rubbed up in a mortar with an equal weight of phosphorus pentachloride. The action was immediate and brisk, and the contents of the mortar became liquid ; but the decomposition was not nearly as violent as when the potassium salt obtained from the diazo decomposition was employed. The liquid chloride mixture was poured into water and thoroughly stirred up. A clear, almost colorless oil gathered on the botton of the vessel. This was washed several times with water, and then placed in a test-tube in a freezing-mixture. It did not solidify. Müller converted the sulphonchloride, which he obtained, into the corresponding acid by heating it with water in a sealed tube. He stated that it did not decompose with water until it was heated to 130°.

About 5 cc. of the sulphonchloride and 100 cc. of water were placed in a flask connected with an inverted condenser and boiled. Considerable bumping occurred, a small portion of the contents of the flask at times fuming out through the top of the condenser. In about an hour and a half the oily liquid had entirely disappeared. The solution was then poured into an evaporating dish and boiled until it attained a syrupy consistency. More water was added and it was again evaporated down. This process was repeated until the solution gave no indication of the presence of hydrochloric acid when tested with silver nitrate. An effort to obtain the metatoluenesulphonic acid in crystalline condition was unsuccessful. After it had become viscous, further heating on a water-bath resulted in giving it a dark, almost black, color. Made clear by boiling with animal charcoal and filtering, it darkened again when kept on the water-bath.

Efforts were then made to crystallize it by evaporation under diminished pressure. About 15 cc. of the syrupy liquid was placed in a round-bottomed flask, which was connected to a filter-pump and kept in boiling water for over an hour. On cooling the contents of the flask remained fluid. The viscous liquid was then placed in a test-tube, and kept in a freezing-mixture for half an hour, and though its temperatnre was lowered to 18° below zero, its condition did not change.

Müller, Von Pechmann, Pagel, and Klason, all obtained, by evaporating down their acid solutions, a syrup which stiffened to a mass of deliquescent crystals.

Barium Salt of Metatoluenesulphonic Acid.—A solution of the acid was heated to boiling, and neutralized with barium carbonate. The solution was then filtered and evaporated down to a small bulk. On cooling, the barium salt crystallized out in minute crystals. With favorable conditions, bunches of apparently rectangular plates about $\frac{1}{8}$ of an inch long, were obtained. It is very soluble in water, insoluble in absolute alcohol and ether; soluble in dilute alcohol, and precipitated from its solution in the latter by the addition of a large quantity of ether.

It contained one molecule of water of crystallization.

The salt was analyzed with the following results:

I. 0.2702 gram of the salt gave off, at 180°, 0.0101 gram of water.

II. 0.2208 gram of the salt gave off, at 180°, 0.0080 gram of water.

III. 0.2702 gram of the salt gave 0.1260 gram of barium sulphate.

IV. 0.2208 gram of the salt gave 0.1030 gram of barium sulphate.

	Calculated for	Found.	
	$(C_6H_4<^{CH_3}_{SO_3})_2Ba+H_2O$.	I.	II.
H_2O	3.62	3.73	3.62
Ba	27.56	27.42	27.42

The barium salt, made by Müller by boiling the free acid with pure barium carbonate, gave off two molecules of water of crystallization. Neither from water nor from alcohol could he obtain it in a distinctly crystalline condition.

Lead Salt.—This salt, which was very soluble in water, and slightly soluble in strong alcohol, was obtained in the form of a mass of crystals consisting of small scales. The addition of a large quantity of ether to its dilute alcoholic solution precipitated it in scales. The analysis of the salt was made with the following results :

For water of crystallization :

I. 0.2480 gram of salt, heated to 160°, gave off 0.0078 gram of water.

II. 0.2394 gram of salt gave off 0.078 gram of water.

III. 0.2212 gram of salt gave off 0.0070 gram of water.

IV. 0.2480 gram of the anhydrous salt gave 0.1278 gram of lead sulphate.

V. 0.3538 gram of the salt gave 0.1813 gram of lead sulphate.

VI. 0.3781 gram of the salt gave 0.1923 gram of lead sulphate.

	Calculated for		Found.	
	$(C_6H_4<^{CH_3}_{SO_3})_2Pb+H_2O$.	I.	II.	III.
H_2O	3.17	3.14	3.17	3.16
Pb	36.33	35.21	35.57	34.74

In describing his lead salt, Müller calls attention to the fact that the anhydrous salt absorbed moisture very rapidly, which made it difficult to get good results for the water of crystallization. No such behavior was noticed in the case of the lead salt here described. The results in water of crystallization agreed as closely as possible with the theoretical, and no difficulty in weighing was experienced. On the other hand, it was found impossible to get good results in the determination of lead. Many analyses were made, the three given above being the best results obtained. Ignition of the salt, alone, or when moistened with sulphuric or nitric acid, invariably caused some reduction. Precipitation in alcoholic solution, as lead sulphate, and filtration through a Gooch crucible, gave no better results.

Calcium Salt.—The calcium salt was made by decomposing finely powdered calcite by means of the free acid. It was extremely soluble in water, and could be obtained in crystalline condition only by evaporating the solution almost to dryness, when, upon cooling, it solidified in a mass of scales, which were so matted together that they could not be obtained in dry condition, by long standing in the air. Upon heating a saturated solution of the calcium salt, a slight milky precipitation occurred, which disappeared on standing, indicating its greater solubility in cold than in hot water. Analyses were made of a specimen which had been dried by standing over sulphuric acid.

I. 0.3989 gram of the calcium salt, heated to 200°, lost 0.0343 gram of water.

II. 0.3196 gram of the calcium salt, heated to 200°, lost 0.0270 gram of water.

III. 0.3989 gram of the salt gave 0.1210 gram of calcium sulphate.

IV. 0.3196 gram of the salt gave 0.1051 gram of calcium sulphate.

	Calculated for	Found.	
	$\left(C_6H_4<\begin{smallmatrix}CH_3\\SO_4\end{smallmatrix}\right)Ca+2H_2O.$	I.	II.
H_2O	8.61	8.59	8.44
Ca	9.57	9.66	9.67

Müller did not succeed in obtaining the calcium salt of his toluenesulphonic acid in crystalline condition from its solution in water, and his salts, whether obtained by evaporating the water solution to dryness or by filtering the boiling alcoholic solution through a warmed filter, continued to give off water when heated to 200°.

The salt, the analysis of which is given above, was easily obtained in crystalline condition, and gave off all its water of crystallization at 180–190°; and heated to 200°, it began to darken in color. It was evidently a different compound from that of Müller.

Sodium Salt.—The sodium salt was made by exactly precipitating the barium by means of sodium sulphate from a solution of the barium salt. It is very soluble in water, from which it crystallizes out in large scales when the solution is evaporated down.

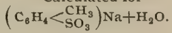
Its analysis resulted as follows:

I. 0.1641 gram of salt lost, upon heating to 150°, 0.0139 gram of water.

II. 0.2060 gram of salt gave off 0.0175 gram of water.

III. 0.1502 gram of the salt gave 0.0549 gram of sodium sulphate.

IV. 0.1885 gram of the salt gave 0.0683 gram of sodium sulphate.

	Calculated for	Found.	
	 $\left(C_6H_4<\genfrac{}{}{0pt}{}{CH_3}{SO_3}\right)Na+H_2O.$	I.	II.
H_2O	8.49	8.47	8.49
Na	10.85	10.91	10.73

The sodium salt obtained by Müller did not crystallize well from water, and contained but one-half a molecule of water of crystallization.

Potassium Salt.—The potassium salt was made, as was the sodium, by the exact precipitation of a solution of the barium salt. This salt crystallized in thin scales and was easily soluble in water, sparingly so in strong alcohol. It dissolved to a great extent in hot, ordinary alcohol, from which it separated out in small scales. Addition of ether to the alcoholic mother-liquor caused a copious precipitation.

The following are the results of its analysis:

I. 0.2146 gram of the salt, heated to 180°, gave off 0.0096 gram of water.

II. 0.1980 gram of the salt gave off 0.0089 gram of water.

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III. 0.2146 gram of the salt gave 0.0844 gram of potassium sulphate.

IV. 0.1980 gram of the salt gave 0.0773 gram of potassium sulphate.

	Calculated for	Found.	
	$C_6H_4<\substack{CH_3\\SO_3K}+\frac{1}{2}H_2O.$	I.	II.
H_2O	4.11	4.47	4.49
K	17.75	17.63	17.50

This potassium salt agrees with that of Müller in solubility and water of crystallization.

Silver Salt.—Pure silver carbonate, obtained by precipitating a solution of silver nitrate by means of sodium carbonate, was decomposed in a boiling solution of the acid. Upon filtering and evaporating down to a small volume, bunches of rectangular plates were obtained, which showed a micaceous cleavage. These were easily soluble in water, and to a much less extent in alcohol. From their solution in the latter they were precipitated by the addition of ether. They contained no water of crystallization, and blackened on exposure to the light.

I. 0.2061 gram of the salt gave 0.0080 gram of silver.

II. 0.2640 gram of the salt gave 0.1023 gram of silver.

	Calculated for	Found.	
	$C_6H_4<\substack{CH_3\\SO_3Ag.}$	I.	II.
Ag	38.71	38.81	38.75

Magnesium Salt.—The magnesium salt was made by boiling pure magnesium carbonate in a solution of the acid. After neutralizing the acid the solution was filtered, and reduced in volume by evaporation. On standing, the salt crystallized out in beautiful, long, transparent, thick prisms, which lost water rapidly in the air. Their crystalline structure appeared to be orthorhombic and hemihedral. The magnesium salt is slightly soluble in alcohol, from which it is precipitated by ether in minute plates. The property of rapidly losing water of crystallization, when exposed to the air, was not noticed in any of the other salts of metatoluenesulphonic acid. But the magnesium salt, which consisted of beautiful, large, transparent crystals, some of them an inch and over in length when first removed from the mother-liquor, became opaque after brief exposure to the air, and disintegrated upon long standing.

Subjected to analysis it yielded the following results:

I. 0.2050 gram of the salt lost, when heated to 150°, 0.0644 gram of water.

II. 0.2166 gram of the salt gave off, at the same temperature, 0.0691 gram of water.

III. 0.2636 gram of the anhydrous salt gave 0.0865 gram of magnesium sulphate.

IV. 0.2797 gram of the anhydrous salt gave 0.0896 gram of magnesium sulphate.

	Calculated for	Found.	
	$\left(C_6H_4<^{CH_3}_{SO_3}\right)_2Mg+10H_2O.$	I.	II.
H_2O	32.05	31.45	31.90
Mg	6.56	6.55	6.40

Manganese Salt.—A solution of the barium salt was treated to exact precipitation with manganous sulphate. On reducing the solution to a small bulk and cooling, the manganese salt crystallized out in long prisms, which were easily soluble in water, and to a slight extent in alcohol. From the alcoholic solution they were precipitated in the form of bunches of small needles.

The following are the results of the analyses:

I. 0.2150 gram of the salt gave off, when heated to 200°, 0.0461 gram of water.

II. 0.2708 gram of the salt gave off 0.0588 gram of water.

III. 0.2150 gram of the anhydrous salt gave 0.0326 gram of manganous manganic oxide.

IV. 0.1689 gram of the salt gave 0.0326 gram of manganous manganic oxide.

	Calculated for	Found.	
	$\left(C_6H_4<^{CH_3}_{SO_3}\right)_2Mn+6H_2O.$	I.	II.
H_2O	21.44	21.44	21.67
Mn	10.89	10.92	10.93

Zinc Salt.—The zinc salt was made by treating a boiling solution of the acid with pure zinc carbonate. After filtering and evaporating down the solution, long, slender prisms were deposited. They were soluble in water and alcohol, and were precipitated from the alcoholic solution in minute scales on the addition of ether. The salt was very stable, and the crystals retained their lustre after long exposure to the air. It was analyzed for zinc, by precipitating as carbonate and igniting.

I. 0.3377 gram of the salt lost, upon being heated to 180°, 0.0695 gram of water.

II. 0.3106 gram of the salt lost, upon being heated to 180°, 0.0638 gram of water.

III. 0.3377 gram of the salt gave 0.0527 gram of zinc oxide.

IV. 0.3106 gram of the salt gave 0.0482 gram of zinc oxide.

	Calculated for $\left(C_6H_4<\begin{smallmatrix}CH_3\\SO_3\end{smallmatrix}\right)_2Zn+6H_2O$.	Found. I.	II.
H_2O	20.97	20.58	20.54
Zn	12.62	12.51	12.52

Copper Salt.—On evaporating a solution of this salt nearly to dryness and cooling, a mass of light blue scales was obtained. The copper salt was very soluble in water and ordinary alcohol, very slightly soluble in absolute alcohol, and insoluble in ether. The addition of ether to an alcoholic solution of the salt caused its precipitation in minute, almost white, scales. No very satisfactory determination of water of crystallization of the copper salt could be obtained.

On heating 0.2995 gram of the salt to constant weight in an air-bath at 170°, it was found to have lost 0.0450 gram of water, or 15.02 per cent. The theoretical percentage of water, assuming the salt to contain four molecules of water of crystallization is 15.03. The determination of the water of crystallization of different specimens obtained by precipitating the salt from its alcoholic solution by means of ether, gave no concordant results.

The copper was determined in the anhydrous salt by electrolysis.

I. 0.2545 gram of the anhydrous salt gave 0.0401 gram of copper.

II. 0.3725 gram of the salt gave 0.0585 gram of copper.

Calculated for $\left(C_6H_4<\begin{smallmatrix}CH_2\\SO_3\end{smallmatrix}\right)_2Cu$.	Found. I.	II.
15.55	15.70	15.70

Metatoluenesulphonanilide.—This substance was made by bringing together some metatoluenesulphonchloride and a slight excess of aniline. The action was extremely rapid. The flask became very hot and its contents solidified to a crystalline mass. The contents of the flask were then boiled with dilute hydrochloric acid, in order to remove any unacted upon aniline, and the anilide was then crystallized from ether, in which it was very soluble. A yield of small prismatic crystals was obtained. The anilide was insoluble in cold water, and dissolved only to a very slight extent in boiling water. It was extremely soluble in alcohol, from which it crystallized out in large monoclinic prisms. It melted sharply at 96°.

Müller and Wiesinger[1] mention a metatoluenesulphonanilide, which melted at 72°. They obtained their meta acid by treating their diazo compound with sulphurous acid.

Metatoluenesulphontoluide.—The ortho- and paratoluides of metatoluenesulphonic acid were made by bringing together metatoluenesulphonchloride and the proper toluidine, the latter in slight excess. The reaction was very rapid and violent, part of the contents of the flask volatilizing. The excess of toluidine was removed by warming the mixture with dilute hydrochloric acid, and washing several times with water. Both toluides are well crystallized compounds, insoluble in water, but very soluble in ether, alcohol, and benzene.

The metatoluenesulphonorthotoluide crystallizes in prisms and thick plates, and melts at 108°.

The metatoluenesulphonparatoluide crystallizes in small prisms and melts at 106°. The toluide mentioned by Müller and Wiesinger[2] melted at 103°.

Conclusion.

From the study of metatoluenesulphonic acid and its salts, we may conclude that the compounds obtained by Müller and others who employed analogous methods for obtaining them, were impure products.

This follows especially from a comparison of the properties of the amide, and from the fact that the sulphonchloride suffers decomposition into the acid when boiled with water in an open vessel, while the sulphonchloride of Müller did not decompose until heated to 130° in a sealed tube.

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[1] Ber. d. chem. Ges., **12**, 1348.

[2] *Loc. cit.*

No detailed comparison of the salts of the metatoluenesulphonic acid herein described, with those made by other methods than those of Müller was made, for previous work in this laboratory, by Fahlberg and Metcalf showed conclusively that they were not true meta compounds.

JOHNS HOPKINS UNIVERSITY,
JUNE, 1895.

Contributions from the Chemical Laboratory of Harvard College.

XCVII.--ON THE COLORED COMPOUNDS OBTAINED FROM SODIC ETHYLATE AND CERTAIN AROMATIC NITRO COMPOUNDS.[1]

BY C. LORING JACKSON AND MARTIN H. ITTNER.

The formation of strikingly colored substances by the action of alkaline solutions on certain aromatic nitro compounds was first mentioned, so far as we can find, by H. Salkowski[2] in his paper on "Chrysanisic Acid," where he described the nearly black compound formed from chrysanisic acid, the reddish purple one from dinitranisic acid and the rose-colored derivative of ethoxydinitrobenzoic ethylester. Hepp[3] also observed the appearance of a blood-red color when symmetrical trinitrobenzol was treated with potassic or ammonic hydrate.

Much more recently, Victor Meyer[4] called attention to the curious phenomena attending the action of sodic hydrate on symmetrical dinitrobenzoic acid, which with one equivalent or less of alkali gave a colorless solution, with more dilute alkali a yellowish-red color, and with an excess of strong alkali a dark violet solution, but this latter color faded in a short time, and the solution became colorless again. After longer standing of the same solution it took on a permanent fuchsine-red color. He connected these phenomena with the colors obtained from symmetrical trinitrobenzol with alkalies, and suggested that the fugitive color might be due to a salt formed through the replacement by sodium of the hydrogen standing upon the benzol ring between the two nitro groups. In continuation of this work Shukoff[5] has studied under Victor Meyer's direction the fuchsine-red solution, and has found that it contains the two new acids, dinitroazoxybenzoic acid and azoxytrihydoxybenzoic acid. Shortly after the appearance of the paper by Victor Meyer, C. A. Lobry de Bruyn[1] published a paper in which he described a series of experiments on these substances begun six years before. These included the observation that nitro compounds, which give the red color with alkalies, are not acted on by metallic sodium, even when the solution in xylol is boiled with it; and that potassic hydrate formed red crystals with a solution of symmetrical trinitrobenzol in methyl alcohol, whereas no such compound was formed with sodic hydrate. He also observed that the formation of the red compound was accompanied or rather followed by that of potassic nitrite. In a later paper Lobry de Bruyn and Van Leent[2] succeed in analyzing these red crystals, which have the formula $C_6H_3(NO_2)_3KOCH_3 \frac{1}{2}H_2O$. In a subsequent paper[3] Victor Meyer points out that this compound can also be considered $C_6H_2K(NO_2)_3CH_3OH \frac{1}{2}H_2O$; and shows that sodic nitrite is not eliminated by the action of sodic hydrate in aqueous solution on symmetrical trinitrobenzol, if the test is made at once, and the alkali is not too strong, thus confirming the observation of Lobry de Bruyn, which is described in the paper[4] just cited. F. H. van Leent[5] has recently analyzed another of these compounds obtained by the action of potassic hydrate in methyl alcohol solution on trinitrobenzoic acid, (CO_2H, $(NO_2)_3$ 1, 2, 4, 6), and found that its formula is

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[1] Part of the work described in this paper was included in a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy, by Martin H. Ittner.

[2] Ann. Chem. (Liebig), **163**, 49, 52, 56.

[3] *Ibid*, **215**, 359.

[4] Ber. d. chem. Ges., **27**, 3153.

[5] *Ibid*, **28**, 1800.

$$(C_6H_2(NO_2)_3COOKCH_3OK)_2CH_3OH.$$

We should perhaps add to the list of these bodies the dark-green compound formed by the action of sodic or ammonic hydrate on bromdinitrophenylacetic acid, discovered by W. S. Robinson and one of us,[6] since there was some evidence that the normal salt of this substance might be colorless, and also the unstable red substance formed by an excess of alkali and dichlordinitrophenylacetic acid observed by W. R. Lamar and one of us.[1] In this latter case a colorless salt was formed when the alkali was not added in excess.

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[1] Rec. Trav. Chim. Pays. Bas., **14**, 89.

[2] *Ibid*, **14**, 150; Ber. d. chem. Ges., '96, R. 40.

[3] Ber. d. chem. Ges., **29**, 848.

[4] Rec. Trav. chim. Pays Bas., **14**, 91.

[5] *Ibid*, **15**, 89.

[6] This JOURNAL, **11**, 553.

Our attention was called to this subject by the discovery of a number of brilliantly colored derivatives from parabromdimetanitrotoluol and related substances. After we had made some progress in the study of these compounds, our work was brought to an end by the paper of Victor Meyer, already mentioned. We accordingly, after some delay, published a notice[2] of what we had done, with the statement that we withdrew in order not to interfere with the chemists, who had already occupied this field. This notice brought us at once a letter from Lobry de Bruyn, in which he told us that Victor Meyer had left to him the study of the colors formed with sodic alcoholates, and in the most generous way asked us to continue our research. We are glad to have this opportunity of expressing our warmest thanks to him for his great courtesy and liberality. Unfortunately, our time was so occupied after we received permission to continue the work, that we could devote only a month to it, but in that time we have collected enough facts to make it worth while to publish this paper, especially as we shall be unable to continue the work together.

The colors discovered by us are collected in the following table, in which the first column gives the formula of the substance, which was converted into the colored compound by the action of a strong alcoholic solution of sodic ethylate, the second the color obtained, and the third the stability, which we have expressed roughly by stating whether the color lasted for several seconds, for several minutes, or under favorable conditions for several hours. The precautions necessary in order to obtain some of these substances will be found in the experimental part of this paper. All these substances have the constitution CH_3 (or COOH) $1.NO_2 3.X 4.NO_2 5$.

Substance.	Color.	Stability.
$BrC_6H_2(NO_2)_2CH_3$	Blue	Seconds
$C_6H_5NHC_6H_2(NO_2)_2CH_3$	Green	Seconds
$NH_2C_6H_4NHC_6H_2(NO_2)_2CH_3$	Green	Seconds
$C_6H_2Br_3NHC_6H_2(NO_2)_2CH_3$	Purple	Minutes

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[1] This JOURNAL, 18, 681.

[2] Ber. d. chem. Ges., 28, 3063.

Substance.	Color.	Stability.
$NH_2C_6HBr_3NHC_6H_2(NO_2)_2CH_3$	Bluish purple	Minutes
$BrC_6H_2(NO_2)_2COOH$	Reddish purple	Hours
$BrC_6H_2(NO_2)_2COOC_2H_5$	Rose	Hours
$C_6H_5NHC_6H_2(NO_2)_2COOH$	Pansy purple	Hours
$C_6H_5NHC_6H_2(NO_2)_2COOC_2H_5$	Cherry red	Hours
$CH_3OC_6H_2(NO_2)_2COOH$	Reddish purple	Hours
$C_2H_5OC_6H_2(NO_2)_2COOH$	Reddish purple	Hours
$C_2H_5OC_6H_2(NO_2)_2COOC_2H_5$	Rose	Hours
$NH_2C_6H_2(NO_2)_2COOH$	Black	
$NH_2C_6H_2(NO_2)_2COOC_2H_5$	Red	

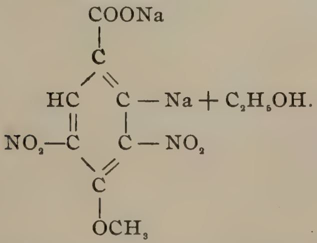
These substances fall into three groups, so far as stability goes. The substituted toluols gave very unstable compounds, which faded usually in about ten seconds, unless one of the substituting radicals was a tribromanilido group, in which case somewhat more stable compounds were formed; but these were far inferior in stability to the derivatives of the substituted benzoic acids, which kept, even when moist, for half an hour or more, and, when purified and dried, lasted often for several days. All of these substances, however, decomposed spontaneously in time, and were almost instantaneously decomposed by water or acids, giving the original substance, unless this had been affected by a secondary reaction.

We succeeded in preparing the colored compound from dinitranisic acid in a state fit for analysis by precipitating the alcoholic solution of it with ligroïn. The analyses of the substance dried *in vacuo* led to the formula

$$C_6H_2OCH_3(NO_2)_2COONaNaOC_2H_5,$$

in the form of which we do not intend to commit ourselves to any theory of the constitution of the substance, but merely to indicate that it amounts to the sodic dinitranisate with the addition of the elements of one molecule of sodic ethylate. If heated to 110° it lost a weight nearly corresponding to one molecule of alcohol, and the residue contained an amount of sodium corresponding to the formula $C_6H_2OCH_3(NO_2)_2COONa_2$. This substance, however, did not dissolve in alcohol with the purple color of the original body, but had a brown color, which indicated decomposition. In one case we thought we detected an odor of formaldehyde, while heating the compound to 110°, but we have never observed it again. In a later determination we collected the substance volatilized, and tested it with ammonic hydrate for formaldehyde. The result showed, that if there was any present, it could not amount to more than one per cent. The principal part of the substance given off was alcohol, to judge from its very evident odor and the iodoform test.

The only theory to account for these products, which has been published in any detail, is that advanced by Victor Meyer, who looked upon them as salts formed by the replacement of an atom of hydrogen on the benzol ring by an atom of sodium or potassium. As stated by him, this hypothesis is not applicable to the substances described in this paper, since he considered that the hydrogen replaced was that standing between the two nitro groups in dinitrobenzoic acid or trinitrobenzol, and none of our compounds contain such an atom of hydrogen, the position between the two nitro groups being occupied by some other radical (Br, C_6H_5NH, CH_3O, or some others), which is not replaced by sodium, as the original substance can be regenerated from the colored compounds without difficulty. A slight modification of this hypothesis, however, renders it applicable to our compounds. This consists in supposing that the hydrogen between a nitro group and the methyl or carboxyl radical is the one replaced by the metal. If this view is adopted, the formula of the compound from dinitranisic acid would become



This hypothesis has much to recommend it, as it would lead us to expect a strongly colored compound, from which water or acid would easily regenerate the mother substance, and that the compounds containing the negative carboxyl would be more stable than those containing methyl. Further the fact observed by us that alcohol is given off on heating this substance seems to indicate that it contains alcohol of crystallization. On the other hand there are observations which tell against this hypothesis; thus according to it we must assume one molecule of alcohol of crystallization in each of the substances analyzed, a similarity of composition, which is certainly improbable in compounds derived from such different bodies; while in regard to the substance analyzed by Lobry de Bruyn and Van Leent, the still more improbable assumption must be made that it contains at the same time alcohol and water of crystallization. A much stronger objection than these, however, exists in the fact observed by Lobry de Bruyn that sodium does not act on trinitrobenzol even at the boiling-point of xylol. In fact this seems almost conclusive against the hypothesis that these bodies are formed by the replacement of hydrogen by sodium.

We have also studied the spontaneous decomposition of the reddish-purple compound derived from bromdinitrobenzoic acid and sodic ethylate. This, when in contact with sodic ethylate, gradually changes without alteration of its color into a mixture of sodic bromide, and the colored compound from ethoxydinitrobenzoic acid. Acidification then gives the parethoxydimetanitrobenzoic acid, which melts at 192°, and had not been made previously, so far as we can find. If the mixture is allowed to stand for a longer time, it is converted into paroxydimetanitrobenzoic acid and sodic bromide. This change is indicated by the dark brown color which the mass assumes.

In the hope of finding an easy method of preparing parethoxydimetanitrobenzoic ethylester, we studied the action of hydrochloric acid and alcohol at 100° on chrysanisic ester, and found that in this way a little of the ethoxy ester and ammonic chloride was formed, but the yield is so small that the process is of no practical value.

EXPERIMENTAL PART.

Description of the Colored Compounds.

From Parabromdimetanitrotoluol, $C_6H_2Br(NO_2)_2CH_3$.—If an excess of a concentrated alcoholic solution of freshly prepared sodic ethylate was poured over a little dry bromdinitrotoluol, at first no marked effect was noticed, but if, after the mixture had stood about two minutes, two or three times as much absolute alcohol was added, and the whole well shaken, the liquid took on such an intense dark blue color as to be nearly opaque. The color thus produced was as vivid as that of the more lively aniline blues. This marked color lasted for about ten seconds, at the end of which time it had entirely vanished, leaving a colorless liquid mixed with unaltered bromdinitrotoluol, which is not easily soluble in alcohol. Further addition of sodic ethylate, alcohol, or bromdinitrotoluol failed to produce a reappearance of the color. We cannot state whether the whole of the bromdinitrotoluol was recovered unchanged; certainly most of it was left in the original condition, but a small part may have undergone some permanent change. This, however, if it took place, did not consist in the removal of the bromine or nitro groups from the molecule, as we could get no test for a bromide or nitrite in the aqueous washings of the residue, if the reaction had been stopped as soon as the color vanished. If, on the other hand, the solution of sodic ethylate was allowed to stand for some time with the bromdinitrotoluol, another reaction set in, as was shown by the formation of an abundance of sodic bromide. The organic products of this second reaction have not yet been analyzed. They are not dinitrocresol (or ethoxydinitrotoluol), as far as we could judge from some preliminary work upon them.

The blue compound described above did not appear unless the conditions given were observed with a great deal of care. Dilution, or the addition of an acid, decolorized it instantly. Sodic methylate gave a similar blue compound, and so did sodic amylate, but this latter was more stable than that derived from the ethylate.

From Anilidodinitrotoluol, $C_6H_5NHC_6H_2(NO_2)_2CH_3$, *Melting-point* 169°.—When an excess of a sodic alcoholate was poured on dry anilidodinitrotoluol the orange crystals became coated with a dark green substance, some of which also dissolved in the alcohol. The color vanished in a very short time, instantly on dilution with a large quantity of absolute alcohol, although the addition of a small quantity intensified the color. *Amidophenyleneimidodinitrotoluol*,

$$NH_2C_6H_4NHC_6H_2(NO_2)_2CH_3,$$

melting-point 185°, gave under the same conditions an exactly similarly-colored compound.

Tribromanilidodinitrotoluol, $C_6H_2Br_3NHC_6H_2(NO_2)_2CH_3$, melting-point 238°, and *tribromamidophenyleneimidodinitrotoluol*, $NH_2C_6HBr_3NHC_6H_2(NO_2)_2CH_3$, melting at 222°, gave with an alcoholic solution of sodic ethylate, the first, a purple color, the second, a bluish-purple color. Both these colors were more stable than those described previously, they lasted longer, and no careful observance of conditions was necessary in preparing them ; in fact colors were obtained with alcoholic potassic hydrate, but not with sodic hydrate. Also the residue left after the alcohol had evaporated gave the color again upon addition of more of the solution of sodic ethylate. The absolute stability of the colors, however, was slight, as they were decomposed on spontaneous evaporation of the solution, and instantaneously by the addition of water or an acid.

From Parabromdimetanitrobenzoic Acid, $C_6H_2Br(NO_2)_2COOH$.—When a strong alcoholic solution of sodic ethylate was added to dry bromdinitrobenzoic acid or one of its salts, an intense reddish-purple color was developed throughout the solution. The color was like that of monomethylrosaniline. This color was formed easily, no precautions being necessary to obtain it, and, as it was very intense, we have used it to advantage as a delicate test for the presence of bromdinitrobenzoic acid. The colored body, like the acid from which it was formed, was easily soluble in alcohol, but could be obtained as a purple crystalline mass by cooling very concentrated alcoholic solutions. It was decomposed instantly by the addition of water, a colorless solution of sodic bromdinitrobenzoate being formed. Acids also decolorized it at once, converting it into bromdinitrobenzoic acid. These observations show plainly that this colored compound was a derivative of bromdinitrobenzoic acid, and this view was confirmed by the fact that no test for sodic bromide could be obtained from the water, which had been used to decompose the color, if it had been applied immediately after its formation. If, on the other hand, the colored compound was allowed to stand for ten minutes, a distinct test for sodic bromide was obtained from the water used to decompose it ; and the amount of this bromine increased with the length of time that the color stood before it was decomposed. As this formation of sodic bromide was accompanied by no perceptible change of color, we are inclined to think that the purple derivative of bromdinitrobenzoic acid decomposed forming sodic bromide and the derivative of ethoxydinitrobenzoic, which has the same color as the original colored substance. The substance retained its reddish purple color for more than half an hour under ordinary conditions. If allowed to stand moist with alcohol for a longer time, a marked change from reddish purple to reddish brown was observed, which was rendered complete by allowing the liquid to evaporate to dryness in the air, or to stand in a corked flask for twenty-four hours. We have succeeded in detecting in this decomposed product, ethoxydinitrobenzoic acid, oxydinitrobenzoic acid, and sodic bromide. The identification of these substances will be discussed in a later paragraph. No test was obtained for sodic nitrite, or for oxalic acid, which would probably have been one of the products, if an azoxy compound had been formed. Sodic methylate behaved like sodic ethylate.

The bromdinitrobenzoic ester, $C_6H_2Br(NO_2)_2COOC_2H_5$, melting at 105°, gave with sodic ethylate in alcoholic solution a beautiful pink color like that of eosine. On standing, this pink color gradually passed into the reddish purple of the derivative from the free acid showing that the ester had been saponified.

Anilidodinitrobenzoic acid, $C_6H_2C_6H_5NH(NO_2)_2COOH$, melting-point 239°, gave with a strong solution of sodic ethylate a bluish purple colored compound, which resembled the the color of a pansy. This substance, which was fairly stable retaining its color for more than half an hour, was very slightly soluble in alcohol, in this respect resembling the acid from which it was obtained. We could not, therefore, prepare it pure, as orange streaks of the sodium salt of the acid were visible even in our most carefully prepared specimens. We tried dissolving the anilidodinitrobenzoic acid in benzol or acetone before adding the sodic ethylate, in the hope of getting a complete reaction, but under these conditions, although the colored substance was formed, it vanished in less than two minutes. That the substance formed from the anilido acid is more stable even than that from the brom acid was shown by the fact that a bluish purple coloration was obtained with aqueous sodic hydrate. The anilidodinitrobenzoic ester, $C_6H_5NHC_6H_2(NO_2)_2COOC_2H_5$, melting at 154°, gave a cherry-red compound with sodic ethylate, which was as slightly soluble in alcohol as the product from the corresponding acid.

Dinitranisic acid $C_6H_2OCH_3(NO_2)_2COOH$, and *ethoxydinitrobenzoic acid*, $C_6H_2OC_2H_5(NO_2)_2COOH$, melting at 192°, gave with an alcoholic solution of sodic ethylate reddish purple compounds similar to that from bromdinitrobenzoic acid; in fact it is probable that the colored product obtained from this latter body is, after the very first, a mixture of the color from the ethoxy acid and sodic bromide. When the colored compound from dinitranisic acid is treated with hydrochloric acid, the dinitranisic acid is regenerated. Both these colors are comparatively stable, keeping in alcohol for over half an hour, and when carefully purified and dried, even for several days. Similar colored compounds were obtained with sodic methylate or alcoholic potash, as was found previously in the case of the dinitranisic acid by Salkowski,[1] who also observed that the ethoxydinitrobenzoic ethylester, $C_6H_2OC_2H_5(NO_2)_2COOC_2H_5$, gave with sodic ethylate a bright red-rose color.[2] This color was so similar to that given by the bromdinitrobenzoic ester, that they could not be distinguished by the eye alone.

Salkowski[3] also stated that chrysanisic acid, $C_6H_2NH_2(NO_2)_2COOH$, was colored almost black by potassic hydrate in aqueous or alcoholic solution. We repeated this work in order to see whether this substance would be adapted for analysis, and to confirm his observations. The yellow crystals of chrysanisic acid, when dropped into an alcoholic solution of sodic ethylate, turned black, and the liquid close to the crystals was seen by the microscope to be dark blue-violet. This color, however, did not spread through the solution, either because the substance was very slightly soluble, or because it was decomposed by the liquid. The chrysanisic ethylester, $C_6H_2NH_2(NO_2)_2COOC_2H_5$, melting at 114°, gave a red color with the alcoholic solution of sodic ethylate similar to that obtained from the anilido ester. Oxydinitrobenzoic acid, melting at 245°–246°, gave no colored compound of this class with sodic ethylate, that we could find, the only product being the brown salt. From mononitranisic acid and nitrosanilidodinitrotoluol also we could not obtain any colored compounds.

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[1] Ann. Chem. (Liebig), **163**, 57.

[2] *Ibid*, 49.

[3] *Ibid*, 52.

Composition of the Colored Compound Made from Dinitranisic Acid and Sodic Ethylate.

After a careful consideration of the colored compounds just described, and a series of experiments, which served to show that many of them were not fitted for analysis, we decided that the one which could be most easily prepared for analysis was that derived from dinitranisic acid.

Preparation of Dinitranisic Acid.—This substance was made according to Salkowski,[1] as follows: Oil of anise was heated with nitric acid of specific gravity 1.4 in a flask, and the product, chiefly mononitranisic acid, after drying, was allowed to stand in the cold for 48 hours with a mixture of nitric acid of specific gravity 1.5, and sulphuric acid. There was a rapid evolution of carbonic dioxide when the substances were mixed, and this could not be prevented by adding the solid in small quantities and careful cooling. The organic product of this reaction was precipitated by pouring the acid liquid into a large amount of cold water, and the precipitate treated with a cold dilute solution of sodic carbonate, which dissolved the dinitranisic acid, but left behind the dinitro and trinitranisol also formed in the process. The dinitranisic acid, precipitated with hydrochloric acid, was purified by recrystallization from dilute alcohol until it melted constant at 179°. The yield obtained by this process is poor, but it is much better than that obtained by acting on bromdinitrobenzoic acid with sodic methylate, as in that case most of the dinitranisic acid was saponified to oxydinitrobenzoic acid during the operation.

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[1] Ann. Chem. (Liebig), **163**, 7.

Preparation of the Colored Compound.—Six grams of the dinitranisic acid were put into a glass-stoppered bottle of 250 cc. capacity, and dissolved in about 20 cc. of absolute alcohol. The sodic ethylate, prepared from 0.5–0.6 gram of sodium and 20–30 cc. of alcohol, was then added, when the purple color appeared immediately. The bottle containing the mixture was shaken and cooled for 20 minutes (if precipitated at once, it is apt to come down in a viscous form), and then 100 to 150 cc. of ligroïn (boiling between 60° and 90°) were added, and the bottle kept cool for one hour, after which the heavy purple precipitate was removed by means of the filter pump, and thoroughly washed with ligroïn. The solid was then transferred to a platinum crucible and dried *in vacuo* over night. In the morning the substance was found partly covered with a brown crust, resulting from the decomposition of a portion of it. This was scraped off carefully, and the purple solid, which showed no signs of decomposition, dried *in vacuo* for about 40 hours in all. During the last five hours it lost less than two milligrams, and accordingly we analyzed it, as we feared it might decompose, if we attempted to dry it more thoroughly. The analyses of this preparation are given under I. and II.

It is obvious that this process could not give a pure product, unless the excess of sodic ethylate used was soluble in the mixture of ligroïn and alcohol and in the pure ligroïn. To satisfy ourselves on this point we had tried the following experiments before we carried through the preparation: Two cubic centimeters of an alcoholic solution of sodic ethylate were mixed with 30 cc. of ligroïn. No precipitate was observed. This showed that we needed not to fear the precipitation of sodic ethylate from its solution; but we felt that another experiment was advisable to determine whether sodic ethylate could be washed out of a precipitate with ligroïn.

Accordingly a concentrated alcoholic solution of dinitrobenzol mixed with a quantity of sodic ethylate was precipitated with ligroïn and thoroughly washed with this solvent. The precipitate was then ignited with sulphuric acid, when no residue of sodic sulphate was obtained. The method, therefore, is capable of giving satisfactory results.

In a second preparation of the colored compound made in the same way none of the brown decomposition-product was observed. This was dried until it lost only 0.0005 gram in three hours. The analyses of it are given under III. and IV.

I. 0.1149 gram of the substance dried *in vacuo* gave on combustion 0.1532 gram of carbonic dioxide and 0.0353 gram of water.

II. 0.3067 gram of the substance gave 0.1334 gram of sodic sulphate.

III. 0.2056 gram of the substance dried *in vacuo* gave 0.2660 gram of carbonic dioxide and 0.0660 gram of water.

IV. 0.4975 gram of the substance gave 0.2194 gram of sodic sulphate.

	Calculated for $C_6H_2OCH_3(NO_2)_2COONaNaOC_2H_5$.	Found.			
		I.	II.	III.	IV.
Carbon	36.15	36.37	....	35.28	....
Hydrogen	3.01	3.41	....	3.56	....
Sodium	13.86	....	14.09	....	14.29

A third preparation made like the preceding was dried over night *in vacuo*, when it was found that like the first it had become partially decomposed. The unaltered purple part was separated from all that had turned brown, and then dried in an air-bath at 110° to constant weight, when it was analyzed with the following results:

V. 0.3371 gram of the substance dried at 110° gave 0.1654 gram of sodic sulphate.

VI. 0.5737 gram of the substance dried at 110° gave 0.2811 gram of sodic sulphate.

	Calculated for $C_6HOCH_3(NO_2)_2COONa_2$.	Found.	
		V.	VI.
Sodium	16.08	15.90	15.88

According to these analyses, therefore, the substance dried *in vacuo* has lost at 110° the elements of one molecule of alcohol. It does not follow, however, that the loss was alcohol itself, and in this analysis during the drying we thought that we detected the odor of formaldehyde. Nor does it follow that the dried substance is closely related to the colored body dried *in vacuo*. In fact its appearance indicated that it had undergone decomposition, as it had a yellowish-brown color and did not give any purple color on the addition of absolute alcohol or of sodic ethylate. The study of this substance must be postponed till a future time.

We made a fourth preparation (as before), and studied this in the hope of determining the nature of the volatile products given off, when the purple substance is heated. This preparation was dried *in vacuo* for about 50 hours, during the last five of which it lost only 0.0012 gram. It showed no signs of decomposition, and a little of it gave a purple solution with absolute alcohol. It was then transferred to a small Erlenmeyer flask, which was connected with a flask containing a one per cent. solution of ammonic hydrate, and a second containing a standard solution of sulphuric acid. The whole was arranged so that a stream of air purified by potassic hydrate and sulphuric acid could be drawn through the apparatus. The Erlenmeyer flask was then heated to about 100° by an oil-bath for an hour, and for a short time even to 130°. Drops of a liquid collected in the connecting-tube leading from the Erlenmeyer flask, which were driven into the ammonic hydrate by a gentle heat. After the apparatus had cooled, the flask containing the ammonic hydrate was stoppered tightly, and allowed to stand in a warm place over night in order that any formaldehyde present might be converted into hexamethylenetetramine. The amount of this substance formed was determined by titration, and indicated that there was a little more than one per cent. Under these circumstances we are inclined to think that no formaldehyde was present, but that this result was due to some slight experimental mistake. We could not detect the smell of formaldehyde in this or any subsequent experiment. On the other hand, the flask, when opened, exhibited a marked smell of ethyl alcohol, which was also very evident after the ammonic hydrate had been neutralized; further a portion of this liquid treated with iodine and potassic hydrate gave a precipitate of iodoform. We infer, therefore, that the substance given off was principally, if not entirely, ethyl alcohol. The following determinations were also made in this experiment:

0.7120 gram of the substance dried *in vacuo* lost 0.1095 gram when heated to 130°.

0.5934 gram of the salt dried at 130° gave 0.2966 gram of sodic sulphate.

	Calculated for $C_6HOCH_3(NO_2)_2COONa_2C_2H_5OH$.	Found.
Alcohol	13.86	15.38

	Calculated for $C_6HOCH_3(NO_2)_2COONa_2$.	Found.
Sodium	16.08	16.19

The per cent. of alcohol found is not so near to that calculated as we could wish, but it is sufficient to confirm the numbers in our other analyses.

The analyses given above were made with four different preparations, and show that the colored compound is formed by the addition of the elements of one molecule of sodic ethylate to one molecule of sodic dinitranisate. The bearing of our observations on the way in which the atoms are arranged in this substance has been discussed as fully as is worth while in the introduction to this paper.

In the hope of throwing more light on this part of the subject, we dissolved some of the purple body in propyl alcohol, intending to reprecipitate it by ligroïn, when the analyses of the precipitate might show whether the alcohol in the original substance was alcohol of crystallization, or more intimately united to the molecule. In the only experiment, for which we had time, the solution of the purple substance in propyl alcohol decomposed before we could reprecipitate it. The experiment will be repeated.

Decomposition of the Colored Compound from Bromdinitrobenzoic Acid.

As has been stated already, the reddish purple compound obtained by the action of sodic ethylate on bromdinitrobenzoic acid decomposed spontaneously, as was shown by the formation of sodic bromide. If this decomposition had run to an end, as for instance when the alcohol mixed with the color was allowed to evaporate spontaneously in the air, or when the compound stood in a corked flask with alcohol for twenty-four hours, the brown product consisted principally of sodic bromide and the sodium salt of paroxydimetanitrobenzoic acid, which was recognized by the melting-point of the acid, 245°–246°. If, on the other hand, the decomposition had not gone so far, a different product was obtained. Thus a portion of the colored compound, which had stood for some time, but still retained its reddish purple color, was treated with dilute sulphuric acid ; this gave a precipitate melting at about 180° and containing halogen. Upon crystallization from very dilute alcohol this proved not to be bromdinitrobenzoic acid, as it seemed at first, but a mixture of this body with another, which, when pure, melted at 192°, and contained no bromine. Upon analysis it proved to be ethoxydinitrobenzoic acid, as shown by the following results :

0.1171 gram of the substance gave on combustion 0.1814 gram of carbonic dioxide and 0.0369 gram of water.

	Calculated for $C_6H_2OC_2H_5(NO_2)_2COOH$.	Found.
Carbon	42.19	42.24
Hydrogen	3.13	3.50

It seems, therefore, that the first products of the spontaneous decomposition of the colored compound from the bromdinitrobenzoic acid are sodic bromide and ethoxydinitrobenzoic acid, which at once combines with more of the sodic ethylate to form the colored compound derived from this acid, since the color does not change. The oxy acid is probably formed by a subsequent reaction from the ethoxy acid. Some analyses of the decomposed, but still colored, compound, showed that all the bromine had passed into sodic bromide, and that the sodium contained in the preparation not in the form of sodic bromide corresponded to that in the colored compound made from ethoxydinitrobenzoic acid.

	Calculated for $C_6H_2OC_2H_5(NO_2)_2COONaNaOC_2H_5$.	Found. I.	Found. II.
Sodium	13.29	13.10	13.26

In other cases less satisfactory results were obtained. We consider these numbers of but little value, because they are analyses of mixtures, but it is interesting to note that they confirm the results of the analyses of the compound from the methoxy acid given earlier in this paper.

The decomposition-products of the compound from sodic methylate and bromdinitrobenzoic acid were similar. They were sodic bromide, dinitranisic acid (paramethoxybenzoic acid), and in extreme cases oxydinitrobenzoic acid. It is possible that from both these compounds other products were formed in small quantities.

Ethoxydinitrobenzoic Acid, $C_6H_2OC_2H_5(NO_2)_2COOH$.—The method of preparing this acid by the action of sodic ethylate on bromdinitrobenzoic acid described in the last paragraph is unsatisfactory, since the yield was very small, a large part of the acid being changed during the process into the corresponding oxy acid, and also since the purification of the product was a very tedious affair. As this ethoxy acid seemed well adapted to the formation with sodic ethylate of a colored compound fit for analysis, we devoted some time to trying to find a good method for preparing it, and give here a description of one of our methods, which is of some interest, although it did not lead to the desired result. This, however, was of little importance, as in dinitranisic acid, we found a more accessible substance as well adapted to our purpose.

This method was founded on the hope that the ethylester of ethoxydinitrobenzoic acid might be made by the violent action of hydrochloric acid on an alcoholic solution of chrysanisic ester (amidodinitrobenzoic ester), the amido group being replaced by the ethoxy radical, and ammonic chloride being formed. Accordingly the alcoholic solution of this ester saturated with hydrochloric acid in the cold was heated to 100° in a sealed tube for five hours. The residue, after the liquid had been evaporated off, was crystallized from ligroïn, which finally gave a substance melting at 114°, and was, therefore, unaltered chrysanisic ester. The first mother-liquors were allowed to evaporate spontaneously, when they deposited, in addition to the yellow crystals of chrysanisic ester, others which were colorless, long, obliquely terminated prisms; these were separated mechanically, and found to melt at 60°. Salkowski gives the melting-point of ethoxydinitrobenzoic ethylester as 59°. The crystals also gave with sodic ethylate the rose-pink color obtained from this reagent, and the bromdinitrobenzoic ethylester. We feel no doubt, therefore, that we obtained the ethylester of ethoxydinitrobenzoic acid by the action of hydrochloric acid and alcohol on chrysanisic acid, but as the yield was very small, the method is of no practical value.

Properties. — The ethoxydinitrobenzoic acid crystallizes from alcohol in long, flat, colorless prisms, terminated by a single plane at an oblique angle. It takes on a faint yellow tinge when exposed for some time to the air. It melts at 192°. It is very soluble in ether, acetone, or ethyl acetate; easily soluble in benzol, or glacial acetic acid; moderately soluble in chloroform, or carbonic disulphide; fairly soluble in cold ethyl or methyl alcohol, more soluble in either of these solvents, when hot; slightly soluble in cold water or ligroïn, more soluble in either, if hot. The best solvent for it is alcohol. Slightly soluble in hot, strong hydrochloric acid; soluble in strong sulphuric acid, or nitric acid. It is soluble in solutions of alkalies, or alkaline carbonates forming its salts. A solution of the sodium salt prepared by adding the proper amount of sodic carbonate to a weighed portion of the acid gave the following characteristic reactions:

Argentic nitrate or *ferric chloride*, white precipitate.

Cupric sulphate, light green, slightly soluble precipitate.

Plumbic acetate, white precipitate, slightly soluble in cold, freely soluble in hot water.

Baric chloride, white precipitate, soluble with tolerable ease.

The sodium salt itself crystallizes in easily soluble yellow needles. The ethoxydinitrobenzoic acid is not a very stable substance, as dilute acids, or alkalies convert it when warmed into oxydinitrobenzoic acid. Ammonic hydrate gives chrysanisic acid with it. The reddish purple compound with sodic ethylate has been already described.

Contributions from the Sheffield Laboratory of Yale University.

XLIX.—ON THE ACTION OF CHLORCARBONIC ETHYL ESTER ON FORMANILIDE.

BY H. L. WHEELER AND H. F. METCALF.

Sixteen years ago Lellmann[1] made the interesting observation that chlorcarbonic ethyl ester reacts energetically with formanilide, while with acet- or benzanilide no reaction was obtained, even on heating under pressure. Lellman isolated and identified diphenylformamidine as one of the products of the reaction. He explained the formation of the amidine by stating that perhaps formylphenylurethane is formed, and that this compound appears to be quite unstable, two molecules breaking up into the amidine, carbon dioxide and ethyl oxalate.

Formylphenylurethane has been prepared by us by the action of chlorcarbonic ethyl ester on phenylimidoethyl formate or ethylisoformanilide. The reaction is precisely similar to the action of other acid chlorides on the isoanilides, and it takes place as follows:[2]

$$C_6H_5N{=}CHOC_2H_5 + ClCO_2C_2H_5 = C_6H_5NCHO.CO_2C_2H_5 + C_2H_5Cl.$$

The products being formylphenylurethane and ethyl chloride. Thus prepared it is an oil which can be distilled with little or no decomposition. It is no more unstable than other mixed diacid anilides, and it does not suffer the above mentioned decomposition. When warmed with acid or alkali, the formyl group is removed and phenylurethane results. It will be shown below that no ethyl oxalate is formed in the action of chlorcarbonic ethyl ester on formanilide, and that therefore Lellmann's explanation is incorrect.

Just recently Freer and Sherman[3] have undertaken a reexamination of this reaction. They isolated the amidine, and state that in addition to this they obtained an oil which was washed with water, and which would not solidify, while "after slight warming it broke down, giving off a gas and changing to diphenylformamidine, thus showing conclusively, according to Wheeler,[1] that it was ethylisoformanilide, $C_6H_5N{=}CHOC_2H_5$."

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[1] Ber. d. chem. Ges., **14**, 2512.

[2] This JOURNAL, **19**, 129.

[3] This JOURNAL, **18**, 579.

If Freer and Sherman had examined the oil more carefully, which is obtained according to their directions, they would have found that it is not ethylisoformanilide. Moreover, it does not contain the slightest trace of this compound. The properties of the oil and the fact that it even partially withstood the treatment it received, show conclusively that it was not ethylisoformanilide. Ethylisoformanilide or phenylimidoethyl formate was first obtained by Comstock and Clapp.[2] These authors describe it, as stated in Beilstein's Handbuch,[3] as an oil boiling from 213° to 215° at 741 mm. pressure.[4] In the article to which Freer and Sherman refer this imido ester was not described as an oil which decomposes on distillation, but which boils at 18 mm. presure at about 106°. Under these conditions it has therefore almost the same boiling-point as its isomeric imido ester, *i. e.*, imido ethyl benzoate.[5]

Ethylisoformanilide and all the other isoanilides prepared in this laboratory[6] differ from the imido esters of Pinner, inasmuch as they cannot be washed with water without decomposition; indeed, on exposure to the moisture of the air, they soon solidify, changing into the corresponding amidines, or regenerating the formyl compound. The peculiar penetrating pleasant odor of the isoanilides, like that of the imidoesters of Pinner, is characteristic and traces of these compounds can readily be detected by their odor. This odor was entirely lacking in the above mentioned oil.

If ethylisoformanilide is formed in the action of chlorcarbonic ester on formanilide, which most probably is the first step of the reaction, its existence would naturally be very brief in the presence of chlorcarbonic ester, and, as shown in this paper, it would further react, not only with the chlorcarbonic ester, giving formylphenylurethane, but also probably with hydrogen chloride and the water, which are formed as by-products.

From this and the following it will be seen that hitherto the only products which have been accurately identified in this reaction are diphenylformamidine hydrochloride and carbon dioxide. By a more thorough examination of this reaction we have obtained the following as final reaction-products: Diphenylformamidine hydrochloride, formylphenylurethane phenylurethane, carbon dioxide, carbon monoxide and ethyl chloride, and the oil which Freer and Sherman state is ethylisoformanilide will be shown in the experimental part of this paper to be a mixture of the nitrogen derivative formphenylurethane, phenylurethane, and any unaltered formanilide. It must also have contained some chlorcarbonic ester when they attempted the distillation. It frequently has a slight odor resembling monochlorethylacetate, which possibly comes from a slight impurity in the carbonic ester. At any rate the quantity of this material is extremely small.

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[1] This JOURNAL, **18**, 381.

[2] *Ibid*, **13**, 527.

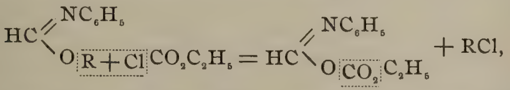
[3] Dritte Auflage, p. 359.

[4] Compare also Claisen: Ann. Chem. (Liebig), **287**, 364.

[5] Bushong: This JOURNAL, **18**, 490.

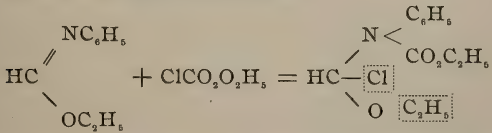
[6] *Ibid*, **12**, 499; **13**, 515, 525.

The formation of the above products would seem to indicate that formanilide and silver formanilide react with chlorcarbonic ethyl ester in the same manner, except that in the case of formanilide the reaction is complicated by the secondary reactions of hydrogen chloride. The products in these two reactions are identical, so that one general equation may represent the primary reaction as follows:



$$\mathrm{HC}\begin{matrix}\diagup\!\!\diagup\,\mathrm{NC_6H_5}\\ \diagdown\,\mathrm{O}\boxed{\mathrm{R+Cl}}\mathrm{CO_2C_2H_5}\end{matrix} = \mathrm{HC}\begin{matrix}\diagup\!\!\diagup\,\mathrm{NC_6H_5}\\ \diagdown\,\mathrm{O}\boxed{\mathrm{CO_2}}\mathrm{C_2H_5}\end{matrix} + \mathrm{RCl},$$

the unstable isodiacid anilide thus formed separating carbon dioxide, which is frequently the case with chlorcarbonic ester reactions, giving phenylimidoethyl formate. Here, however, it has only a brief existence, as it immediately reacts with the chlorcarbonic ester, giving formylphenylurethane and ethyl chloride as follows:[1]



$$\mathrm{HC}\begin{matrix}\diagup\!\!\diagup\,\mathrm{NC_6H_5}\\ \diagdown\,\mathrm{OC_2H_5}\end{matrix} + \mathrm{ClCO_2O_2H_5} = \mathrm{HC}\begin{matrix}\diagup\,\mathrm{N}<\begin{matrix}\mathrm{C_6H_5}\\ \mathrm{CO_2C_2H_5}\end{matrix}\\ -\boxed{\mathrm{Cl}}\\ \diagdown\,\mathrm{O}\ \boxed{\mathrm{C_2H_5}}\end{matrix}$$

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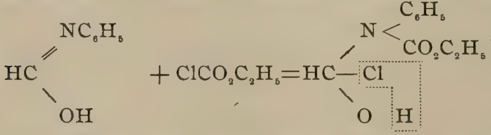
[1] In the case of the silver salt a small amount of ethylisoformanilide was actually isolated. It is therefore evident that the chlorcarbonic ester has a greater tendency to react with the silver salt than with the isoanilide, while in the case of formanilide the facts are the reverse.

On the other hand, the ingenious suggestion of Freer and Sherman to account for the formation of ethylisoformanilide, may represent the primary course of the reaction if formanilide has the structure $\underset{\searrow\!\!\!\searrow O}{HC}{-}NHC_6H_5$. They assume that the chlorcarbonic ethyl ester adds on the nitrogen, which then becomes pentavalent, and the addition-product thus formed decomposes into the imido ester, carbon dioxide and hydrogen chloride. It is to be noticed that if the reaction takes place in this manner, it is analogous to the action of other acid chlorides on the anilides, at least in regard to the formation of an intermediate pentavalent nitrogen addition-product.[1]

At any rate, there is little doubt that phenylimidoethyl formate is the first product of the reaction. Wallach[2] has shown that hydrogen chloride converts formanilide into diphenylformamidine hydrochloride, possibly as follows:

$$2C_6H_5NHCHO = C_{13}H_{12}N_2HCl + CO + H_2O.$$

This and the fact that the isoanilides are converted into amidines by hydrogen chloride[3] accounts for the formation of carbon monoxide and the amidine hydrochloride in the above reaction. The formation of carbon monoxide may also be due to the displacement of the formyl group, as formyl chloride, which decomposes into the oxide and hydrogen chloride.[4] Formylphenylurethane may be a secondary product and result from the action of the chlorcarbonic ester on the isoanilide first formed, or it may be a primary product as follows:



$$HC\begin{cases} {=}NC_6H_5 \\ {-}OH \end{cases} + ClCO_2C_2H_5 = HC\begin{cases} {-}N<\begin{matrix}C_6H_5\\CO_2C_2H_5\end{matrix} \\ {-}Cl \\ {=}O \quad H \end{cases}$$

its formation then being analogous to that of the diacid anilides from the silver salts[5] and from the isoanilides[6], Phenylurethane naturally results from formylphenylurethane, since all mixed diacid anilides, by treatment with acids, first liberate the lower acid radical.

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[1] Pictet: Ber. d. chem. Ges., **23**, 3015.

[2] *Ibid*, **15**, 208.

[3] Comstock and Kleeburg: This JOURNAL, **12**, 493.

[4] Compare Pictet: *Loc. cit.*

[5] Wheeler and Boltwood: This JOURNAL, **18**, 381.

[6] Wheeler and Walden: *Ibid*, **19**, 129.

Thus it will be seen that the formation of all the products of the action of chlorcarbonic ethyl ester on formanilide can readily be explained whether formanilide, as its name implies, is an anilide with the structure $HCO.NHC_6H_5$, or whether it has the imido structure and is phenylimidoformic acid. Its structure cannot, therefore, be determined by the final reaction-products in this case, but the analogy which this reaction shows with that of the silver salt is strongly in favor of the imido formula.

The recent work bearing on the structure of formanilide appears to favor the view that this compound is an imido acid. Cohen and Archdeacon[1] conclude from their interesting work on sodium alcoholate addition-products of the anilides, that the structure of formanilide and indeed also of other anilides is best represented by the imido formula.

Claisen,[2] on the other hand, has recently given what at first sight appears to be a strong argument for the amide structure, *i. e.*, that the sodium salts of the true oxymethylene compound, oxymethylene camphor, for example, give O-esters with ethyl iodide, while formanilide does not. He carries, however, this analogy, or lack of analogy, too far when he states that if formanilide has the structure $C_6H_5N{=}CHOH$, it should boil lower than its O-ethyl derivative, $C_6H_5N = CHOC_2H_5$, while the fact is that formanilide boils higher.

He arrived at this conclusion from a consideration of the boiling-points of the following compounds :

	B. P.		B.P.
Oxymethylene camphor	251°	O-Ethyl derivative	270°
Oxymethylene-acetoacetic ester	200°	O-Ethyl derivative	266°
Oxymethylene-acetylacetone	190°-200°	O-Ethyl derivative	257°

The objection to this reasoning is that the above compounds do not contain the nitrogen-carbon grouping $—N{=}CHOH$ in question, but the carbon-carbon grouping $={C}{=}CHOH$, which is assumed to be analogous without sufficient reason. For it might be argued that compounds containing the nitrogen-carbon grouping $—N{=}CHOH$ would show differences in the boiling-points similar to those containing the oxygen-carbon grouping $O{=}CHOH$, that is that the imido acids and their esters would be expected to correspond with the simple acids and their esters, and, since the acids boil higher than their esters and formanilide higher than its ester, the structure $C_6H_5N{=}CHOH$ is the correct one for formanilide.

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[1] J. Chem. Soc. (1896), 91.

[2] Ann. Chem. (Liebig), **287**, 360.

For example:

	B. P.		B. P.
$O{=}CHOH$	99°	$O{=}CHOC_2H_5$	54°.4
$O{=}C(CH_3)OH$	118°	$O{=}C(CH_3)OC_2H_5$	77°
$O{=}C(C_6H_5)OH$	250°	$O{=}C(C_6H_5)OC_2H_5$	213°
$C_6H_5N{=}CHOH$	294°	$C_6H_5N{=}CHOC_2H_5$	212°

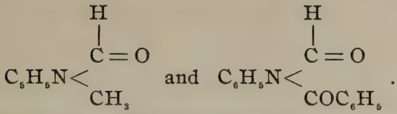
Similar reasoning to that which has led Claisen to consider formanilide as an anilide may be employed to show that it is not. For if instead of drawing conclusions in regard to its structure from comparison of compounds containing the group $=C{=}CHOH$ with their ethyl esters, a comparison is made of compounds containing the group $\equiv C{-}CHO$, with what theoretically would be their O-derivatives, we find that the compounds with the true formyl group, in this case also, boil lower than the O-ethyl derivatives. Therefore, since the boiling-point of formanilide does not correspond with this series, formanilide must have the imido structure.

For example:

	B. P.		B. P.
$H_3C{-}CHO$	20.°8	$H_2C{=}CHO{-}C_2H_5$	35.°5
$(CH_3)_2CO{-}CHO$	63°	$(CH_3)_2C{=}CHOC_2H_5$	92°–94°
$CH_3(C_2H_5)CH{-}CHO$	90°	$CH_3(C_2H_5)C{=}CHOC_2H_5$	111°
$C_6H_5NH{-}CHO$	294°	$C_6H_5N{=}CHOC_2H_5$	212°

This shows that there is no analogy to be expected between the boiling-points of oxymethylene derivatives containing the group $=C{=}CHOH$ with formanilide. On account of the relation which exists between the boiling-points of acids and their esters, and since formanilide or phenylimidoformic acid and its ester show this same relation, the conclusion to be drawn (if any) from the boiling-points is that formanilide has the imido structure.

Although the group $-N{=}CHOH$ may exist in formanilide, it cannot exist in the secondary anilides, that is, in such compounds as methyl formanilide, or in the diacid anilides, benzoyl formanilide, for example. These compounds must have the structure,



$$C_5H_5N<\begin{matrix}\overset{\displaystyle H}{\overset{|}{C}}=O\\ CH_3\end{matrix} \quad \text{and} \quad C_6H_5N<\begin{matrix}\overset{\displaystyle H}{\overset{|}{C}}=O\\ COC_6H_5\end{matrix} \; .$$

Auwers[1] has found that formanilide shows in its cryoscopic behavior a departure from the formyl secondary anilides. This, as Auwers states, may be due to some unknown cause, and not necessarily result from the presence of hydroxyl in formanilide.

It is interesting also to note that formanilide as first shown by Comstock and Kleeburg, readily forms a silver salt, while acet- and benzanilide apparently do not. It may be stated in general that formanilide is far more reactive than the other anilides. These facts would seem to indicate that formanilide has the imido structure, and therefore reacts with chlorcarbonic ethyl ester in the manner first stated above.

EXPERIMENTAL PART.

Action of Chlorcarbonic Ethyl Ester on Formanilide.

On mixing chlorcarbonic ethyl ester and formanilide, an absorption of heat takes place, the formanilide slowly dissolves, and, at 23°, a slow evolution of gas soon takes place. At 60° to 70° the evolution of gas is rapid, while on the water-bath it may become violent, as Lellmann observed.

The Liquid and Solid Products.—60 grams of formanilide and 54 grams of chlorcarbonic ethyl ester were mixed and warmed until solution took place, and the reaction was well started. After a short time the material was placed in a desiccator over lime until the odor of the ester had disappeared. It was then taken up in ether and separated from the diphenylformamidine hydrochloride which remained. This residue was dissolved in water and precipitated by ammonia, when it melted at about 136°. The ethereal solution was washed with water, until all the amidine salt was removed; it was then dried over calcium chloride and the ether evaporated. This then gave the oil which has been stated contains ethyl oxalate and ethylisoformanilide. A portion of this was shaken with strong ammonia; it then showed no signs of alteration and no oxamide was obtained. Ethyl oxalate could not, therefore, have been present. Another portion was shaken with dilute hydrochloric acid; the remaining *oil* was extracted with ether and the aqueous acid solution was then found to contain nothing but a trace of aniline hydrochloride. Since no amidine was formed by this treatment, the absence of ethylisoformanilide in this oil is established. The remaining portion of the oil, which had not been treated with ammonia or acid, and which had a slight odor resembling monochlorethyl acetate, but none resembling ethylisoformanilide, was then subjected to distillation. Unsuccessful attempts were previously made to solidify this oil by freezing. On distilling, it all boiled over at 14 mm. pressure from 159° to 165° without showing any signs of decomposition, at least the amount of gas given off, as stated by Freer and Sherman, was so insignificant that the pressure remained constant during the entire distillation. The residue was also insignificant and diphenylformamidine was not formed. The oil was again distilled at 15 mm. pressure. It then boiled for the greater part from 162° to 164°. On further distilling it showed signs of decomposition, the boiling-point rose to 170°, and in the receiver a trace of a sharp odor, probably of phenyl isocyanate, was noticed. The distillate remained as an oil on cooling. It was then boiled with sodium hydroxide in dilute alcoholic solution, in order to decompose formylphenylurethane into phenylurethane. On cooling, an oil separated, which when treated with dilute hydrochloric acid, solidified in a freezing-mixture. On crystallizing this material from dilute alcohol, it melted at 52°, and in all its properties was identical with phenylurethane.

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[1] Ztschr. phys. Chem., **12**, 711; and **15**, 43, 49.

Phenylurethane is one of those substances which when melted, or when separated from an alcoholic solution, may remain liquid for a long time. Formanilide also belongs to this class of substances which when impure are difficult to solidify, while formylphenylurethane is an oil. Mixtures of the above substances would not therefore be expected to completely solidify or readily to deposit crystals on cooling.

In another experiment where the action was more complete and no formanilide apparently was present, a portion of the oil did solidify on cooling, and this was found to be phenylurethane. On boiling the whole with sodium hydroxide, and then cooling, it apparently solidified completely, giving only the urethane. This shows that the oil was undoubtedly mostly formylphenylurethane, and the oil which Freer and Sherman obtained must have contained the above mentioned substances along with some chlorcarbonic ester, since they state that on warming it gave off a gas, and they obtained more amidine, that is, in their case, the reaction was not completed at first.

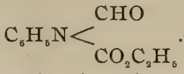
In another experiment, using two molecules of formanilide to one of chlorcarbonic ethyl ester, the products were the same. Hence naturally the oil contained a large amount of formanilide. The greater portion of this was separated by concentrating the ethereal solution when the formanilide separated as an oil, which on standing crystallized. The ethereal filtrate from this gave an oil which boiled for the most part at 14 mm. pressure from 147° to 151°. The observed boiling-point of formylphenylurethane in the same apparatus at 15 mm. pressure was 149° to 151°, while phenylurethane boiled at 151°, and formanilide at 165°–166°. Since in the above reaction hydrogen chloride is formed, and this converts the formylphenylurethane into phenylurethane, the oil is therefore always a mixture of these compounds, and it contains in addition any unaltered formanilide. Since the boiling-points of these substances lie so closely together, attempts to isolate formylphenylurethane, free from admixture, in this case were abandoned. The oil was then converted into the urethane by boiling with sodium hydroxide, and the product thus obtained was a mixture of urethane and formanilide.

Formanilide and phenylurethane in the absence of formylphenylurethane, *i. e.*, after boiling with sodium hydroxide, etc., can readily be separated. When such a mixture is crystallized from quite dilute alcohol, formanilide first separates, while when the mixture is treated with ligroïn it is the phenylurethane that is extracted.

A better yield of the oil can be obtained by carrying out the reaction in benzene.

The Gaseous Products.—The gases were collected over water and examined as follows: The carbonic acid and ethyl chloride were removed together with cold dilute solution of sodium hydrate; the presence of carbon dioxide was then shown in the usual way. On warming this solution ethyl chloride was given off. This burned with a greenish flame, and was shown to contain chlorine by passing the gas over heated calcium oxide, dissolving in nitric acid and precipitating with silver nitrate. Separate experiments under the same conditions with chlorcarbonic ester and boiling sodium hydrate gave no burnable gas. Carbon dioxide and ethyl chloride are the chief constituents of the gaseous products. After the sodium hydrate solution and then cold water failed to diminish the volume of gas, a cuprous chloride solution in hydrochloric acid was run into the burette. This absorbed the greater part of the remaining gas, thus showing the presence of carbon monoxide, the comparatively small part not absorbed was air which had accidentally entered in handling the products.

The results of the above experiments serve to identify the following compounds: Diphenylformamidine hydrochloride, formylphenylurethane, phenylurethane, carbon dioxide, carbon monoxide and ethyl chloride.

Formylphenylurethane, 

$C_6H_5N<\begin{matrix}CHO\\CO_2C_2H_5\end{matrix}$.—This diacid ester anilide was not obtained free from formanilide or phenylurethane when chlorcarbonic ethyl ester acted on formanilide. It can be obtained pure, however, from ethylisoformanilide and chlorcarbonic ethyl ester as follows:

16 grams of ethylisoformanilide were treated with a slight excess, over one molecule of the ester, a lively reaction took place (requiring the use of a return-condenser). Heat was evolved and a stream of ethyl chloride escaped. The reaction was complete in a short time. The whole was then placed over lime in a desiccator until the odor of chlorcarbonic ester disappeared. It was then distilled, and after fractioning, a portion was obtained boiling from 149° to 151° at 15 mm. pressure. This did not solidify on cooling, and on analysis the following results were obtained:

	Found.	Calculated for $C_{10}H_{11}NO_3$.
C	62.67	62.18
H	5.98	5.69
N	7.55	7.23

When the analyzed material was boiled with alkali it decomposed with the separation of the lower acid group, giving phenylurethane. When it was mixed with phenylhydrazine, it soon solidified ; the solid was washed with ether, and this then left pure α-formylphenylhydrazine, melting at 140°. These results show that formylphenylurethane has the structure above assigned to it, both acid groups being attached to nitrogen.

NEW HAVEN, DEC., 1896.

NOTES OF STUDENT WORK FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, UNIVERSITY OF VIRGINIA.

COMMUNICATED BY F. P. DUNNINGTON.

XX.

162.—DRYING AND DELIQUESCENCE OF CERTAIN SALTS.

BY F. W. SMITHER.

Having in view the selection of a substance which is well adapted to use as an absorber of water in an hygrometer, these several salts were chosen as not prone to corrode organic matter or to decompose upon prolonged exposure to a dry or moist atmosphere, and it was proposed to make some determinations of their relative power of absorbing and retaining moisture.

Shortly after having begun this work I saw a notice of a paper by Dr. H. Wilson Hake, read before the Chemical Society of London, Feb. 6, 1896, upon "The Absorption of Moisture by Deliquescent Salts," but, inasmuch as I had then already observed larger absorption of water than was there noted, these results suggested the propriety of continuing this investigation for a greater length of time, aiming thus to ascertain what limits, if any, exist in the absorption of water by such substances.

Each of the salts employed was made from the corresponding carbonate and the amount present was determined in the form of sulphate from similar portions of the solutions used.

Drying of Certain Salts.

In order to ascertain the amount of water retained by these salts when dried in a steam-bath : A definite portion of each was placed in a weighed beaker of about 100 cc. capacity, together with 20 grams of coarsely powdered glass. The glass sufficed to absorb the solution and so secure a better exposure of the salt. These were then dried in a steam-bath at a temperature of 97–98° C., and thus heated for from six to eight hours, cooled, and weighed, kept in a desiccator over night, and re-heated the next day. The daily heating of these salts was continued until the changes which took place appeared well defined. The weights are shown in Table A.

Table A.

	Residues left upon drying.				
Salts anhydrous.	LiCl. 0.2135	$CaCl_2$. 0.2864	CaN_2O_6. 0.4349	$MgCl_2$. 0.1907	MgN_2O_6. 0.3840.
After 1st day	0.2250	0.3758	0.5087	0.2693	0.4791
" 2nd "	0.2212	0.3605	0.5053	0.2649	0.4547
" 3rd "	0.2212	0.3531	0.4908	0.2579	0.4500
" 4th "	0.2212	0.3252	0.4807	0.2527	0.4411
" 5th "	0.2162	0.3214	0.4727	0.2499	0.4317
6–10 "	0.2171	0.3372	0.4862	0.2471	0.4380
11–15 "	0.2121	0.3210	0.4758	0.2345	0.4104
16–20 "	0.2128	0.3186	0.4654	0.2274	0.3929
21-25 "	0.2148	0.3265	0.4648	0.2228	0.3858
26–30 "	0.2155	0.3244	0.4626	0.2184	0.3689
30th "	0.2132	0.3200	0.4550	0.2136	0.3458

After the 5th, I have for brevity given only the average weight for each five days, sufficing to show the very slow rate at which some of the water is to be removed. In the latter portion of this experiment the salts of magnesia had lost acid to a small extent, as was indicated by the separation of a white insoluble crust of magnesium hydrate, the amount of which was estimated at the close. Many years ago it was observed that these magnesium salts could not be rendered anhydrous without this decomposition.

The considerable surface of glass exposed in obtaining these weighing will account for a slight variation in the weights and toward the close of the experiment, no doubt, some water was re-absorbed each night from the calcium chloride of the desiccator. Therefore, a few of the weights which appeared decidedly inaccurate were omitted in making up the averages given.

From this work the following observation may be made:

Lithium chloride is soon rendered anhydrous and is unaltered upon further heating in the steam-bath, but it is exceedingly hygroscopic at common temperatures.

Calcium chloride, upon the fifth heating, retained less than 1 molecule of water, and thereafter it lost and regained a small fraction of this repeatedly.

Calcium nitrate, upon the fourth heating, retained 1 molecule of water and subsequently it gave up a portion of this very slowly.

Magnesium chloride, upon the second heating retained 2, and upon the nineteenth retained 1 molecule of water, beyond this point it gradually lost acid.

Magnesium nitrate, upon the first heating, retained 2, upon the eighth, 1 molecule of water, and thereafter gradually lost water and a little acid forming some magnesium hydrate as above.

The Absorption of Water.

A similar set of beakers were filled with similar amounts of the several salts used above. In each of these was placed a piece of flat cotton lamp-wick of about two square inches, which sufficed to absorp the solution and afford a greater exposure of the salt. The beakers were placed under a bell-jar of 12 gallons capacity, the atmosphere of which was charged with water from 2 flat dishes, exposing 57 square inches surface of water. Subsequently, a number of estimations were made of the dew-point of the atmosphere within this jar after standing twenty-four hours, which proved to be from 2.0 to 3.5° C. below the temperature.

Each day, when the weighings were made, the atmosphere within the jar was replaced by that of the room, so that for a portion of each day these salts were exposed to the dryer atmosphere of the room.

These experiments were conducted in a protected room, where the temperature varied but little from day to day. The temperature at the time of weighing is given in the table.

The absorptions for the first day were observed upon the specimens which had been long dried at 97° C. upon glass, of which the magnesium salts were in small measure decomposed as stated above.

All the remaining observations of this series were made upon similar portions of the same salts, perfectly neutral, absorbed upon cotton-wick, and brought to the degree of moisture at which the previous samples were substituted.

There was an unimportant inaccuracy in respect to the time, in that there were but six days in the seventh "week," and but five in the eighth "week."

These beakers containing the salts were weighed almost daily for seven weeks, and thereafter weekly, and the weights of water absorbed are indicated in Table B.

Table B.

	Amounts of water absorbed.					
Salts	LiCl.	$CaCl_2$.	CaN_2O_6.	$MgCl_2$.	MgN_2O_6.	
Anhydrous	0.2135	0.2864	0.4349	0.1907	0.3840	Temp.
Water retained	0.0000	0.0336	0.0201	0.0229	0.0277	°C.
After 2 hours	0.063	0.128	0.093	0.100	0.111	19
" 4 "	0.101	0.173	0.127	0.138	0.134	20
" 6 "	0.137	0.210	0.163	0.159	0.157	20
" 8 "	0.176	0.243	0.193	0.178	0.176	22
" 10 "	0.206	0.268	0.216	0.204	0.192	23
" 24 "	0.451	0.519	0.366	0.332	0.335	25
" 2 days	0.750	0.721	0.533	0.544	0.704	20
" 3 "	0.923	0.876	0.642	0.641	0.848	20
" 4 "	1.079	0.997	0.750	0.731	0.978	20
" 5 "	1.195	1.092	0.828	0.792	1.073	23
" 6 "	1.300	1.165	0.892	0.847	1.139	25
" 7 "	1.409	1.206	0.923	0.893	1.170	23
" 2 weeks	2.095	1.540	1.246	1.490	1.521	20
" 3 "	2.495	1.868	1.554	1.682	1.828	20.5
" 4 "	2.647	1.919	1.637	1.667	1.931	17
" 5 "	2.713	1.875	1.658	1.594	1.968	17.5
" 6 "	2.717	1.783	1.624	1.481	1.951	17.5
" 7 "	2.782	1.817	1.662	1.494	1.995	18
" 8 "	2.888	1.876	1.743	1.626	2.029	20.5
" 9 "	3.098	1.994	1.883	1.630	2.205	15.5
" 10 "	3.186	1.966	1.916	1.659	2.262	14.5
" 11 "	3.269	1.994	1.940	1.664	2.301	16
" 12 "	3.327	2.127	2.055	1.778	2.463	12

It appears that when the atmosphere is nearly saturated with moisture, these salts continue to absorb water, and most conspicuously, lithium chloride takes up more than fifteen times its weight. During the sixth week the lithium chloride ceased to absorb and the other salt lost water. I can only explain this by the possibility of the water supply under the bell-jar becoming exhausted. Water was added from time to time, but it was never noticed to have thus dried up.

The amounts of water absorbed are thus found to be far in excess of the figures reported by Dr. Hake in the article above referred to. In each case the water taken up in one week was not half of what was absorbed in the subsequent eleven weeks.

As to the formation of any definite hydrate, the number of molecules of water present at each observation has been calculated in Table C. For the sake of uniformity in valency, the calculations are made for a double molecule of lithium chloride.

Table C.

	Molecules of water absorbed by one molecule of each salt.				
	Li_2Cl_2.	$CaCl_2$.	CaN_2O_6.	$MgCl_2$.	MgN_2O_6.
Molecular weight	85.	111.	164.	95.	148.
Water at beginning	0.00	0.72	0.42	0.63	0.59
After 2 hours	1.39	2.72	1.95	2.76	2.37
" 4 "	2.23	3.72	2.66	3.82	2.86
" 6 "	3.03	4.53	3.41	4.41	3.36
" 8 "	3.89	5.24	4.05	4.93	3.67
" 10 "	4.57	5.77	4.53	5.64	4.10
" 24 "	9.98	11.15	7.67	9.16	7.16
" 2 days	16.60	15.54	11.16	14.98	15.07
" 3 "	20.41	18.88	13.45	17.75	18.15
" 4 "	23.86	21.48	15.71	20.24	20.94
" 5 "	26.43	23.44	17.35	21.93	22.97
" 6 "	28.75	25.10	18.69	23.43	24.39
" 7 "	31.15	26.00	19.33	24.71	25.05
" 2 weeks	46.25	33.19	26.11	41.25	32.56
" 3 "	55.19	40.27	32.56	46.54	39.14
" 4 "	58.55	41.27	34.30	46.13	41.35
" 5 "	60.02	40.40	34.74	44.12	42.14
" 6 "	60.11	38.43	34.02	40.98	41.77
" 7 "	61.43	39.14	34.83	41.34	42.71
" 8 "	63.88	40.42	36.52	45.00	43.44

	Molecules of water absorbed by one molecule of each salt.				
	Li_2Cl_2.	$CaCl_2$.	CaN_2O_6.	$MgCl_2$.	MgN_2O_6.
Molecular weight.	85.	111.	164.	95.	148.
After 9 weeks	68.52	42.98	39.45	45.11	47.20
" 10 "	70.46	42.26	40.14	45.91	48.44
" 11 "	72.33	42.97	40.65	46.06	49.24
" 12 "	73.60	45.82	43.15	49.20	52.72

An examination of these results exhibits no defined cessation in absorption, unless there is a tendency for calcium chloride to form a hydrate with 40 molecules of water. Hence it must be admitted that if any definite hydration in the solution takes place, such combination is so feeble that it would require a carefully maintained temperature and degree of humidity in the surrounding atmosphere to render it possible of recognition. And it is concluded that these salts do not form any hydrates when in the liquid state, at common temperature.

163.—ANALYSIS OF A VARIETY OF ILMENITE.

By George M. Peek.

This mineral, received from Dr. Thos. K. Terrell, of Lynchburg, is found in Bedford Co., Va., about one mile from Forest Depot, N. & W. R. R. It occurs enclosed in a vein of quartz, in plates 1 cm. or more in thickness, cleaves well in one direction and less readily in another, at an angle of 45°; crystallization probably tetragonal, brittle, hardness = 5.25, not magnetic, sp. gr. = 4.699, fusibility = 5, and upon analysis presents the following composition:

		Molecular ratio.
TiO_2	63.31	3.16
FeO	35.99	2.00
MgO	0.82	0.16
SiO_2	1.25	
	101.37	

This composition affords approximately the formula 2(FeO), 3(TiO_2), or $Fe_2Ti_3O_8$, which lies between that of typical Ilmenite 2(FeO), 2(TiO_2), and that of Iserite (Janovsky): 2(FeO), 4(TiO_2).

164.—"MINERAL TALLOW" FROM DANBY, VERMONT.

BY L. E. SMOOT.

Through the kindness of Mr. J. J. Cochrane, of Dorset, Vt., a specimen of this substance has been received. In a limestone cavern near Danby and about 12 miles from Rutland, Vt., this peculiar deposit is found on the walls, in a layer 2 or 3 inches in thickness. It is of a soft, smooth, putty-like consistency, nearly white, and an occasional slight increase in admixed dust shows that it has been formed in layers, each 1 or 2 mm. thick. When allowed to dry, it hardens to a pith-like mass, but upon being again moistened, resumes its original consistency. Under a magnifying power of 412 diameters, it exhibits no crystallization, but is seen as an aggregation of exceedingly minute rod-like particles, suggesting some forms of bacteria, and with this there are some thin films of irregular rounded shapes affording colors (of thin films). When heated in a closed tube, it chars and affords a small amount of alkaline vapors.

An analysis of the clean, white portion by Mr. Smoot shows the following composition :

		Dried.
Lime	7.63	52.19
Magnesia	0.04	0.27
Carbon dioxide	6.04	41.31
Silica	0.52	3.57
Water, lost in desiccator	84.37	....
" " at 130° C.	1.01	....
Organic matter (by diff.)	0.39	2.66
Nitrogen	....	(0.053)
	100.00	100.00

The absence of crystallization suggests that this small portion of organic matter takes an important part in determining the nature of the deposit. The proportion of mineral matter does not greatly differ from that secreted by the oyster, in which the average per cent. of organic matter constitutes but 2.39 of the total dry matter, against 2.66 in the present instance. The amount of nitrogen is smaller, but this would naturally be the first element to be lost upon decomposition of organic matter. Probably, therefore, this large amount of calcium carbonate has been secreted by some minute form of life.

165.—ANALYSIS OF DOLOMITIC MARBLE FROM TEXAS, MD.

BY GEORGE G. BUCK.

For many years this marble has been extensively quarried and is specially valued by reason of its uniform compactness and hardness above that of most other marble.

An average sample taken from the stone employed in building the depot at Glyndon, W. Md. R. R., affords the following results. It has a faint yellow tint, hardness = 3.5, sp. gr. = 2.865, and its composition is :

		Molecular ratio.
Lime	31.58	8.02
Magnesia	19.64	7.04
Ferrous oxide	0.14	0.03
Carbon dioxide	47.55	15.44
Silica	1.27	
	100.18	

Which result shows that it approximates fairly to a true dolomite.

166.—ANALYSIS OF AN ALUM WATER FROM LEE CO., VA.

BY L. E. SMOOT.

This water is from a spring on the farm of Dr. J. E. Browning, 9 miles north-west of Jonesville, Lee Co., Va. It is odorless, colorless, with a decided acid reaction and strong alum taste. Temperature at spring, 70° F. Upon analysis it is found to contain in 1 liter :

	Gram.
Alumina	0.891
Ferric oxide	0.120
Soda (and trace potash)	0.060
Sulphuric oxide	2.530
Nitric acid	0.006
Silica	0.108
	3.715

From which we calculate. One pint contains

	Grains.
Aluminum sulphate	21.805
Ferric sulphate	2.190
Sodium sulphate	1.015
Sulphuric acid, free	1.598
Nitric acid	0.050
Silica	0.788
	27.446

This peculiarly large amount of aluminum sulphate seems worthy of note. This water is about twice the strength of the strongest alum water of Stribling Springs, Augusta Co., Va., which in other respects it much resembles.

167.—ANALYSES OF INFUSORIAL EARTH.

By F. W. Smither.

On the northern bank of the Rappahannock river, at Greenlaw's wharf, in King George Co.. Va., there is a bank of Tripolite about 30 feet in thickness, most of which is of a light-brown color and some of it is almost pure white. A specimen of the latter was examined and appeared under the microscope to consist almost exclusively of perfect infusorial shells containing comparatively little of fragments and extraneous matter. For this reason it was thought well to make an analysis of it.

In connection with this an analysis was also made of a specimen from a similar bank of Tripolite on the Patuxent River, in Calvert Co., near Anne Arundel Co., Md., which is of a pale gray color and consists largely of perfect infusorial shells.

A similar examination was also made of the earth from the well-known bed in Richmond, Va. The sample taken from President's Hill is of a light-brown color.

These three deposits lie in a line running north-east from Richmond and about 40 miles apart.

In the endeavor to estimate the proportion of the infusorial shells it was found that a 30 per cent. solution of sodium hydrate, at 100° C., required about two hours to remove all the shells. A 20 per cent. solution did not dissolve all in six hours. In each case the solvent was allowed to act until, upon examination with the microscope, infusorial shells were no longer to be seen.

Analyses of these specimens afforded:

	Rappahannock.	Richmond.	Patuxent.
Silicon, amorphous	65.83	51.67	48.58
Silica, crystallized	14.65	23.56	35.23
Titanic oxide	0.40	0.64	0.60
Ferric oxide	2.34	2.79	1.20
Alumina	4.17	10.25	5.20
Magnesia	0.71	0.69	....
Lime	trace	0.27	0.25
Water at 100°	4.13	4.73	5.09
Water and organic matter, by ignition	7.50	5.45	4.22
	99.73	100.05	100.37

This analysis verifies the unusual purity of the specimen from Rappahannock, which was first observed.

THE PROTEOSE OF WHEAT.

By Thomas B. Osborne.

In this Journal, Vol. 19, page 65, in a paper on "Alcohol Soluble Proteid of Wheat," Mr. G. E. Teller, after stating that he had found in saline extracts of wheat flours, considerable quantities of the proteid gliadin, says: "Apparently it was this body which was found by Osborne and Voorhees in their salt solution extracts and was designated by them as a proteose and proteose-like body under captions V and VI."

Mr. Teller has assumed without reason that gliadin, as described by me and Mr. Voorhees, is *wholly* insoluble in 1 to 10 per cent. sodium chloride solutions and also that proteoses of wheat are completely precipitated by adding alcohol to 75 per cent. Both of these assumptions are unfounded, and therefore it is not surprising that he obtained reactions for both gliadin and proteose in the 74 per cent. alcohol solution which he expected would contain only gliadin. Furthermore, as he points out, many of the reactions of gliadin are very likely those given in text-books for proteoses, but in our investigation of this seed, we were not misled by this fact, for we expressly called attention, page 404, Vol. 15, to differences which we found between gliadin and the proteose there described.

Mr. Teller has overlooked the fact that we separated the proteids from our extract by saturating with ammonium sulphate, a process which rendered the gliadin insoluble in the strong saline solution in which the other proteids were subsequently redissolved.

In extracts made with salt solutions from which the proteids were separated without previous precipitation with ammonium sulphate, we found gliadin and recognized its presence without difficulty. Further, the proteose which we described, we separated as such from the extracts, and could therefore by no possibility have mistaken gliadin for it.

LABORATORY OF THE CONNECTICUT
AGRICULTURAL EXPERIMENT STATION.

REVIEWS.

AN INTRODUCTORY COURSE OF QUANTITATIVE CHEMICAL ANALYSIS, WITH EXPLANATORY NOTES AND STOICHIOMETRICAL PROBLEMS. BY HENRY P. TALBOT, PH.D., Associate Professor of Analytical Chemistry in the Massachusetts Institute of Technology. New York: The Macmillan Co. 1897.

At the sight of a new manual of chemical analysis one involuntarily exclaims "were there not already enough?" It may be said of most handbooks of qualitative and quantitative analysis that they simply embody the author's method of teaching the subject, and serve mainly the purpose of aiding him in the instruction of his own classes. Teachers have now-a-days come to attach great importance to methods and sequence in teaching, and are perhaps too apt to everlook the fact that success is less due to methods than to the direct impulse and inspiration which they give to their pupils through their personal influence.

But we find in Professor Talbot's Introductory Course to Quantitative Chemical Analysis something more than a book for local use. There is an idea running through it that is more or less new in books of this kind, and one which instructors will heartily welcome. The earnest and thorough teacher cannot see without regret his laboratory classes grow in size beyond his ability to deal with each student individually, and he tries to discover some means whereby he can manifold himself. This may in some degree be accomplished by additional instructors, but they bring inevitably a disturbing element into personal instruction. In Professor Talbot's book there is an attempt to give the student not only the important and essential things which he should know in special cases, but what is of more importance so to direct his thoughts toward his work that he shall grasp the fundamental ideas governing chemical analysis. In other words, the directions and explanations are such as the thoughtful and conscientious teacher would give to his pupil in the laboratory in endeavoring to make him think intelligently for himself.

For example, in the section describing the method for the gravimetric determination of iron there is first given the "procedure" or minute directions for the successful precipitation from a solution of ferrous ammonium sulphate of ferric hydrate, and the subsequent ignition of the precipitate. Then follow eight "notes" giving the reasons for the different steps and the precautions which must be observed in order to secure accuracy of result. It is these notes which give the greatest value to the book, since they direct the student's attention to the great number of variables concerned, even in the simplest chemical analysis. It is safe to say that when a student has performed a few analytical processes under guidance as thoughtful and thorough as this, he will become not merely an accurate worker, but what is of infinitely more importance, a clear thinker and close observer.

The stoichiometrical problems are well chosen and will prove helpful to many a busy teacher. T. M. D.

A SIMPLE METHOD OF WATER ANALYSIS, ESPECIALLY DESIGNED FOR THE USE OF MEDICAL OFFICERS OF HEALTH. BY JOHN C. THRESH, M.D. (VIC.), D.SC., (Lond.), D.P.H., (Camb.) 1897. London: J. & A. Churchill.

This little book explains a method for the chemical examination of water, as respects its fitness for ordinary domestic use, which has been worked out with a good deal of ingenuity, so as to avoid for the analyst multiplied weighings or the preparation of the volumetric solutions generally employed. It is proposed to accomplish this result by the use of "soloids" —evidently similar to the "compressed tablets" so much used for hypodermic medication in this country—each of which contains a definite, very small amount of a particular reagent, and "capsules," each containing in like manner a definite, small amount of the Nessler test solution. Under pressure as to time, or when deprived of the resources of a regularly equipped laboratory, the analyst would no doubt find these "soloids" and "capsules" convenient, though it may well be doubted whether some of those mentioned could be depended upon to keep without alteration for any considerable time. There is risk that the results of a "cut and dried" system of water analysis may have undue weight attached to them, or, on the other hand, that such an analysis may come to be regarded too much as a proper form to be gone through with, though leading to no particular practical conclusions. It is only fair, however, to say that the author of this little work in his introduction points out the superior importance of submitting the source of a water to sanitary inspection rather than merely analyzing the water itself, and elsewhere suggests the chief use of the latter proceeding as indicating the degree of need for the former. J. W. M.

THE GASES OF THE ATMOSPHERE. THE HISTORY OF THEIR DISCOVERY. BY WILLIAM RAMSAY, F.R.S., Professor of Chemistry in University College, London. Macmillan & Co. 1896.

Professor Ramsay describes his book as one written for those who are "without any special scientific training." There is no doubt, however, that chemists will be as ready as others to acknowledge their debt to one who has brought together, in a book of convenient size, the principal facts connected with the history of scientific research upon the composition and properties of the atmosphere.

The book may be divided into two parts, in the first of which are described the discovery of the complex nature of the atmosphere and the isolation of the various constituents, whose presence was recognized prior to 1894. The author starts out by discussing the three principal causes for the tardy recognition of the nature of the air, *viz.*, (1) the confusion of gases with one another; (2) erroneous ideas regarding the phenomena of combustion; and (3) the lack of attention to changes in weight accompanying chemical action. These points are then illustrated in the erroneous conclusions so frequently drawn from their experiments by even such brilliant thinkers as Boyle and Mayow, Black and Priestley, Scheele and Cavendish. Looking back in the light of modern knowledge, one is tempted to underestimate the real genius of the experimenter in view of the unproved and frequently illogical position he was led to assume. As Professor Fitzgerald has recently said of certain other scientific deductions "they are almost taken for granted as a natural possession of the human mind. We are inclined rather to think our predecessors must have been blind not to see such obvious things than to credit the discoverers with preternatural insight."

The author takes up in order the conjectures of Boyle, built as they were in large measure upon the metaphysical reasoning of the Schoolmen; the extraordinary insight of Mayow into the true nature of the process of oxidation—a thoughtful, original investigator, a full century before his time—and the experimental results of Hales, which did not, nevertheless, entirely free his mind from the notion of the identity of all gases. The development of the theory of phlogiston by Stahl is followed by accounts of the discovery of carbon dioxide by Black, and of nitrogen by Rutherford. Next is a chapter upon the discovery of oxygen by Scheele and Priestley and the overthrow of the phlogiston theory through the researches of Lavoisier. Finally, the first part of the book closes with an account of the researches of Cavendish—among others, the discovery of the composition of water and the analysis of the air.

The second part enumerates the facts which led to the discovery and isolation of argon, gives in detail the properties of that gas, and discusses the relation of the substance to the general system of the elements. In the course of these chapters Professor Ramsay disposes very completely of the notions that argon is an allotropic form of nitrogen, and that it is a mixture. He also finds no evidence in favor of the existence in the gas of molecules of different degrees of complexity. A possible explanation of the fact that the atomic weight of the gas is apparently about two units higher than that corresponding to its probable position in the system, is then given. It may be stated thus: The "atomic weight" of an element capable of forming compounds is, as we know it, not necessarily a true measure of its atomic mass, but is the resultant of the several forces acting upon the atom while in combination. Chief perhaps among these is the attraction of gravitation, but this does not act alone: intramolecular forces tend to decrease its effect. Hence the true atomic weight of such an element is possibly somewhat greater than the weight we measure; the difference between the two varies somewhat in individual cases, and, therefore, the differences between the atomic weights as determined for the elements in a given group vary irregularly about a mean value approximately 16 in the first three series. On the other hand, in the case of elements like argon and helium, apparently incapable of forming compounds, the determined atomic weight may be a true measure of the atomic mass, since intramolecular forces have no existence.

Finally, it may be said the book is well abreast of the times. It is eminently readable and its interest is heightened by the introduction of a number of portraits. W. W. R.

A MANUAL OF QUANTITATIVE CHEMICAL ANALYSIS FOR THE USE OF STUDENTS. BY FREDERCIK A. CAIRNS, A.M. Third Edition. Revised and enlarged by Elwyn Waller, Ph.D. 8vo. 417 pp. New York: Henry Holt & Co. 1896. Price $2.00.

The manual is designed "to assist beginners in the practice of quantitative analytical chemistry,'' and to serve at the same time, as a reference book for more advanced analytical chemists. The first twenty pages are devoted to such detailed suggestions bearing upon the operations of quantitative analysis in general, as are likely to prove helpful to the beginner; these are followed by nine typical analyses of simple bodies, and these, in turn, by directions for the analyses of thirty more complex substances, including minerals, ores and industrial products, comprehending, in all, a considerable variety of determinations. The present (third) edition has been enlarged to 417 pages (the first edition contained 270 pages). A number of the chapters have been re-written and expanded, and chapters relating to the analysis of chromite, aluminum bronze, and commercial nitrates have been added, while the chapters relating to the analysis of superphosphates and acetates of lime, guano, raw and refined sugar, flour, milk, turpentine, soap, and petroleum, which are found in the earlier edition, have been omitted from this later one. Still other chapters of the earlier edition are unaltered, or are changed only by the addition of a note at the close.

About forty pages of the material treating of the '' Properties of Precipitates, etc.,'' written by the editor, have been added to the appendix in this edition. This material, the author states, is intended to serve as a substitute for the subject matter included under ''Forms'' in Fresenius' Quantitative Analysis, and to have the advantage over the latter, of greater convenience for reference. The classification of properties adopted to accomplish this end does not seem to be altogether fortunate, and the statements of many of the properties, as given, are inexact, and would sometimes be misleading to the beginner. By a more complete compilation of recently published data to supplement those given by the older authority, and greater care with respect to accuracy of statement, the author would have imparted to his work a far greater value.

The wide range of analyses presented offers a liberal course of instruction in inorganic quantitative analysis, and the procedures have, with few exceptions, if any, been wisely selected for that purpose. The same tendency toward inexactness already noted is occasionally evident through the book, and the diction is not always as smooth as might be desired. It is doubtful if the work is sufficiently comprehensive and authoritative to satisfy the needs of the analytical chemist in active practice, as a reference book. H. P. T.

OBITUARY NOTE.

EUGEN BAUMANN.

Eugen Baumann, the distinguished professor of chemistry in the medical faculty of the University of Freiburg, Germany, died Nov. 30, at the age of 50. Baumann began his career as an apothecary, but soon entered the University of Tübingen, and took up work under the direction of Hoppe-Seyler, who was then professor of physiological chemistry there. In 1872, when Hoppe-Seyler was called to Strasbourg, Baumann went with him as his first assistant. In 1877 Baumann was called to Berlin to take charge of the chemical division of the Physiological Institute. Here he remained until 1883, when he went to Freiburg as the successor of Von Babo, and there he remained until his death.

Baumann's work has been, for the most part, in the field of physiological chemistry, although he has also been active in pure chemistry, though, even in this field, the problems that specially interested him were such as had a direct bearing upon physiology. His last important contribution was the discovery that iodine is a never-failing constituent of the thyroid gland, that it is present in the gland in the form of an organic compound, and that this substance containing iodine is the "active principle" of the preparations made from the gland, and used in medicine.

In the course of his studies of cystin he took up the investigation of the mercaptals and mercaptols, and thus he was led to the discovery of the well-known compounds, sulphonal and trional, which have proved of such great value in medicine. Among the many problems upon which he has worked with marked success, the following may be mentioned: The complex sulphuric acids in urine; the transformations of aromatic compounds in the animal organism; the active condition of oxygen; the presence of glucose in normal urine.

I. R.

OF THE
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Contributions from the Chemical Laboratory of the Case School of Applied Science.

XXIII.—ON THE BUTANES AND OCTANES IN AMERICAN PETROLEUM.[1]

BY CHARLES F. MABERY AND EDWARD J. HUDSON.

As one of us (C. F. M.) has shown,[2] the form of the butanes and octanes in American petroleum is not so well understood as that of other constituents of the series C_nH_{2n+2}. Concerning the butanes, except that an analysis of a gas condensed at 0° by Ronalds gave the composition required for butane, very little has been published beyond the fact that distillates have been collected at 0° and at 8°–9°. It, therefore, seemed advisable to devote some time to the separation of the butanes for the purpose of ascertaining with greater precision what hydrocarbons with these boiling-points are actually contained in petroleum.

The Butanes.

The early investigations of Pelouze and Cahours[3] indicated the presence of butane in their most volatile distillates. A portion collected between 5° and 10° gave with chlorine a "chlorbutyl," boiling-point 65°–70°. In a higher distillate, whose boiling-point was not given, amyl hydride was suspected by the formation of a "chloramyl" boiling at 98°–103°, but this hydrocarbon was not further identified. In the first analysis of the gas from Pennsylvania petroleum, Ronalds[1] condensed an oil at 0°–1°, specific gravity 0.6000 at 0°, that gave the composition required for butane. Ronalds also collected an oil between 6° and 8°, specific gravity 0.6004, vapor density 2.178, which he regarded as a mixture of butane with higher constituents. As will be shown in this paper, nothing further has been done toward verifying the pentane from which the pentyl chloride of Pelouze and Cahours was obtained, although it was really derived from the pentane boiling at 30°, as we have ascertained after many trials.

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[1] Presented to the American Academy of Arts and Sciences, October, 1896. Aid in the work described in this paper was given by the Academy from the C. M. Warren fund for original research.

For efficient aid in the work of this paper, I should acknowledge my obligations to Mr. W. H. Whitfield, who selected portions of the work on the butanes as the subject of a thesis for a degree of Bachelor of Science, and to my assistants, Messrs. C. A. Soch and E. Davidson.—C. F. M.

[2] Proc. Am. Acad., **31**, 23.

[3] Compt. rend., 1862, p. 1241.

Probably on account of difficulty in procuring an adequate supply of materials, Warren[2] gave less attention to the butanes than to the higher constituents. He collected a distillate at 0°, which, on the basis of Ronald's determination, he assumed was a butane. After repeated and careful distillation through his regulated condenser, Warren also separated a liquid, boiling-point 8°–9°. Although nothing further was done towards determining its composition, Warren believed this body "to have been sufficiently purified to justify the conclusion supported by analogy that there is a constituent boiling at about 8°–9°." Since no other attempts have been made to identify the butanes, further study of these bodies was evidently necessary.

In returning to this subject, we assumed at first that it would only be necessary to enforce the results already obtained, which seemed to be supported by our first determinations.[3] But as the work progressed, it soon became evident that this assumption would not be justified. Taking advantage of the extremely cold weather in January, 1895, through the kindness of Messrs. Schofield, Shirmer, and Teagle, we procured 45 liters of a second distillate of the naphtha from Pennsylvania and Ohio petroleum, the most volatile portion that could be condensed with the atmospheric temperature below 0° F. Since the naphthas from Pennsylvania and Ohio petroleum are redistilled together, it is difficult to procure this portion from either crude oil unless, indeed, a run of the crude oil were made in the refinery with this object in view. But this did not seem necessary, since there can be little doubt that the constituents of the most volatile portion of Ohio and Pennsylvania petroleums are identical. During the continued cold weather of January, February, and March of the same year, distillation of this product was continued through a Warren condenser, filled with a freezing-mixture, and the temperature of the distillates was kept very low to avoid loss so far as possible. In this manner a long series of distillations was carried on with small loss, aside from transference, except of the most volatile distillates. In these volatile portions, —20° to —10°, the distillation proceeded from the heat of the surrounding atmosphere, and it was regulated by cooling the still. The results obtained in the study of these distillates were so unexpected, that the entire process of distillation was repeated several times during the colder months of the present year until in all 250 liters of 88°- and 92°- gasoline have been distilled, the portions below 12°, twenty times. The interesting results in the distillations of the present year, especially in excluding a butane at 8°–9°, are due to the patience and care of Mr. Whitfield.

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[1] J. Chem. Soc., 1865, p. 54.

[2] Proc. Am. Acad.. **27**, 56.

[3] *Ibid*, **31**, 23.

In studying the derivatives of these hydrocarbons, the chlorine substitution-products were first formed by bringing together chlorine and the vapor of the hydrocarbon. The method we employed differed somewhat in details from the method of Schorlemmer.[1] In the reaction between chlorine and the hydrocarbon, the intensity of light must be carefully regulated. In direct sunlight so much heat is developed that a flame appears with the separation of carbon. On a cloudy day the action proceeds slowly, and with less light it is suspended. We obtained the most satisfactory results both as regards the progress of the reaction and the yield of the monochlorine derivative in clear sunshine with a sheet of newspaper interposed. In all our distillates the action of chlorine has proceeded with great readiness in the cold. The distillates collected below 0° were well cooled by means of a freezing-mixture. The condensation of the chlorinated product was more complete in a capacious bottle,—a 2-liter bottle for 100–200 cc. of the oil, with the delivery tube extending half way from the top of the bottle to the surface of the liquid. The heavier chlorine comes into intimate contact with the vapor of the oil, and the product condenses for the most part on the side of the bottle. Some of it unavoidably escapes with the hydrochloric acid, and it may be condensed in part by placing in front another bottle well cooled, or, still better, by passing the escaping gas into water. We have not found it essential to separate by distillation the chlorinated product from the hydrocarbon until the action was finished. If it be stopped with a small amount of the hydrocarbon unchanged, which may easily be determined by experience, the product is nearly all the monochlorine compound. The use of iodine suggested by Schorlemmer has not seemed essential, at least in the formation of the butane derivatives, since, without it, there is no difficulty in obtaining 80 per cent. of the monochlorine compound, the remainder consisting for the most part of unchanged hydrocarbon, nor in our experience is the yield increased by the use of iodine. In the separation by fractional distillation of the products of the chlorination, our experience is not in accordance with that of Schorlemmer, who stated that neither the chlorides nor the acetates could be separated by distillation. With long continued distillation, as our results will show, the crude product of the chlorination can be separated into its constituents sufficiently to yield constant boiling-points and satisfactory analytical data.

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[1] Phil. Trans., **162**, 111 (1872).

Since Beilstein[1] found that isobutane boils at —17°.5, it seemed reasonable that it should be contained in our product —10°, especially since a considerable portion of this distillate condensed below —15°. In submitting 200 grams of this distillate in several portions to the action of chlorine with all possible precautions, a considerable portion of the chlorine product was lost, probably because it consisted to a large extent of the more volatile chlorine derivatives of propane. Although much of the unchanged hydrocarbon must have escaped with the gaseous hydrochloric acid, 100 grams remained after the chlorination, which was washed, dried and distilled. Prolonged distillation, however, failed to collect any considerable portion within sufficiently close limits to indicate the presence in appreciable quantity of an individual hydrocarbon. A small quantity, perhaps 5 grams, collected between 65° and 70°, doubtless isobutyl chloride from isobutane, which had not been completely removed into the higher fractions at 0°. But the product distributed itself along in degree fractions from 30° to 150°, at no point in quantities larger than half a gram or 1 gram.

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[1] Ann. Chem. (Liebig), 144, 10.

Between —10° and —2° much smaller quantities of the hydrocarbon distillates were obtained, but within the limits —2° and 2°, 300 grams came together, and the distillate— 0°-1° gave, as its specific gravity at 0°, 0.6029, and at —12°, 0.6141. Ronalds found as its specific gravity 0.6000. A vapor-density determination gave the following value :

0.0945 gram oil gave 73.6 cc. vapor at 5°, under 370.4 mm. of mercury.

Calculated for C_4H_{10}.	Found.
2.01	2.07

In quantities of 100 grams each, the fractions —20° to 2° were converted into the chlorine derivatives. The chlorination of such a quantity is of necessity somewhat tedious ; it requires continuous operation during ten or twelve days, and it cannot be hastened, since too rapid absorption generates heat, and rapid escape of hydrochloric acid carries off the product. With care we were able to complete the absorption of sufficient chlorine without any considerable loss. In subjecting the chlorine product to fractional separation, after the fifth distillation it began to collect between 65° and 70°, and after the twentieth, 80 per cent. collected at 68°-69°. Of the remainder, 40 grams below 60° proved to consist mainly of unchanged hydrocarbon with sufficient chlorine product to raise the boiling-point. Distillation of the higher portions was continued in 1° fractions to 160°, beyond which very little remained. To prevent a slight decomposition above 150°, at first distillation was conducted *in vacuo*, but the boiling-points soon fell below the point of decomposition. In this entire series of 1° distillates, only at 120°–121° did any appreciable quantity collect, and here only to the extent of 2–3 grams. The portions collected at other points were doubtless mixtures in very small amounts of higher chlorine products. The liquid 68°–69° was shown by analysis and vapor density to have the composition required for monochlorbutane.

I. 0.1288 gram oil gave 0.2440 gram CO_2 and 0.1166 gram H_2O.

II. 0.2025 gram oil gave 0.3845 gram CO_2 and 0.1778 gram H_2O.

III. 0.2537 gram oil gave 0.3950 gram AgCl (Carius).

IV. 0.2645 gram of the oil gave 0.4078 gram AgCl.

	Calculated for C_4H_9Cl.	Found.			
		I.	II.	III.	IV.
C	51.89	51.65	51.77	....	....
H	9.73	10.05	9.76	....	....
Cl	38.38	....	....	38.50	38.13

In a determination of its specific gravity at 24°, this butyl chloride gave 0.8690; at 27°.8, another determination gave 0.8648. The latter value agrees closely with that of Pierre and Puchot,[1] who found at 27°.8, 0.8650.

In determining its vapor density by the method of Hofmann, 0.0975 gram oil gave 65 cc. vapor at 100°, under a tension of 36.44 mm.

Calculated for C_4H_9Cl.	Found.
3.20	3.30

In further evidence of its identity, this butyl chloride was converted into the acetate by heating it twenty-four hours to 140° with fused potassic acetate and glacial acetic acid, according to the method of Schorlemmer. Upon diluting the contents of the tube, the oil which separated distilled for the most part at 116°–117°, corresponding to the boiling-point of isobutyl acetate, 116°.5. The acetate was converted into the alcohol by heating with alcoholic potassic hydrate, and its boiling-point, 107°–108°, showed it to be isobutyl alcohol, boiling-point 108°–109°. Upon analysis the alcohol gave the required percentages of carbon and hydrogen:

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[1] Ann. Chem. (Liebig), **163**, 276.

0.1737 gram substance gave 0.4090 gram CO_2 and 0.2113 gram H_2O.

	Calculated for C_4H_9OH.	Found.
C	64.86	64.22
H	13.51	13.52

Isobutyl sulphide was also prepared by boiling the chloride with an alcoholic solution of potassic sulphide. It gave the required percentage of sulphur:

0.1640 gram oil gave, by the method of Carius, 0.2631 gram $BaSO_4$.

	Calculated for $(C_4H_9)_2S$.	Found.
S	21.92	22.03

As already explained, prolonged fractional distillation failed to show the presence of any other chlorine derivative of this hydrocarbon except one that distilled tolerably constant at 121°–122°. The quantity of this product was too limited to admit of complete purification; while the analyses showed that it still contained monochlorbutane, the results are sufficiently close to establish the presence of dichlorbutane. Since no dichlorbutane with this boiling-point has hitherto been found, it is to be regretted that our supply of material was so limited. But on account of the vast amount of labor that would be necessary to obtain an adequate quantity, it has not seemed of sufficient importance in the pressure of other portions of this work.

This substance gave the following results on analysis:

I. 0.1390 gram oil gave by combustion with plumbic chromate 0.1960 gram CO_2 and 6.1887 gram H_2O.

II. 0.2360 gram oil gave 0.5245 gram AgCl.

	Calculated for $C_4H_8Cl_2$.	Found.	
		I.	II.
C	37.79	38.46	....
H	6.30	7.08	....
Cl	55.91	....	54.94

The quantity of this product was insufficient for a determination of its specific gravity. The following value was obtained as its vapor density:

0.1655 gram oil gave 87.2 cc. vapor at 182°, under a tension of 447 mm.

Calculated for $C_4H_8Cl_2$.	Found.
4.39	4.16

Our first attempts towards separating the butanes were made before the necessity of long continued distillation was fully appreciated. Not until after several trials was it observed to what an extent a small proportion of isobutane depressed the boiling-point of pentane. In the earlier work, after 6 or 8 distillations, the product was assumed to be sufficiently pure for chlorination. A study of the chlorine derivative showed beyond question that the hydrocarbon was pentane. We were still further misled by the boiling-point of the pentyl chloride, 96°, which did not correspond to that of any hitherto published. Referring to our former notes on the vapor density of the distillate 8°–9°, we found the following determinations :

I. 0.1717 gram oil gave 45.5 cc. vapor at 16°, under a tension of 48.1 cm. of mercury.

II. 0.0849 gram oil gave 46.8 cc. vapor at 18°.5 ; tension, 47.75 cm.

III. 0.0999 gram oil gave 51.5 cc. vapor at 18°.5 ; tension, 51.75 cm.

IV. 0.0751 gram oil gave 43.5 cc. vapor at 18°.5 ; tension, 45.76 cm.

Calculated for		Found.			
C_4H_{10}.	C_5H_{12}.	I.	II.	III.	IV.
2.01	2.49	2.04	2.38	2.35	2.36

It will be seen that determination I corresponds closely to the composition of butane, and determinations II, III, and IV to that of pentane. When these determinations were made we expected results that would substantiate what had previously been done on the butanes, and therefore accepted only the first result, which was the last one obtained as supporting this view. But in the light of further knowledge of these bodies, the determinations thought to be erroneous correspond more nearly to pentane, although showing the influence of the small quantity of isobutane. The first result was published in a former paper,[1] when it was assumed that we had in hand the butane which Warren had previously separated. Suspecting, therefore, the purity of our hydrocarbon distillate 8°–9°, in resuming this work the distillation was conducted with a sufficient quantity of material, and carried far enough to separate completely all fractions between 5° and 20°. In the fraction 8°–9°, after the tenth distillation, two vapor-density determinations gave, (I) 2.17, (II) 2.17. In a distillate 6°–8°, Ronalds[2] obtained as its vapor density 2.178, evidently indicating, as our values do, a mixture of butane and pentane.

But continuing this distillation in single-degree fractions, scarcely anything remained within these limits after the twentieth distillation. Having obtained the same result in several quantities of 45 liters each, collected at different dates, it became evident that neither Pennsylvania nor Ohio petroleum contains a single body with a boiling-point within these limits. Furthermore, we have not been able to detect normal butane in any of these volatile distillates. There is not the least difficulty in separating chlorine derivatives of these hydrocarbons by fractional distillation. All the chlorine products we have prepared have collected readily within the limits of temperature of their characteristic boiling-points. But in no instance in the chlorination of hydrocarbon distillates collected between —10° and 20° has a distillate collected at 77°–88°, the boiling-point of normal butyl chloride. Having excluded a constituent of Pennsylvania and Ohio petroleum within the limits mentioned above, and having observed that certain properties of isopentane derivatives are not in all respects identical with those previously published, it seemed to us of sufficient interest to devote some attention to the derivatives of this hydrocarbon. We therefore collected several hundred grams of a distillate at 29°–30°, and exposed the oil to the action of chlorine in several separate quantities until about 200 cc. of the substitution-product was obtained. In generating such large quantities of chlorine, without discomfort from leaks, we have found the large Berlin porcelain stills extremely convenient. The chlorinated product was washed, dried, and carried through a long course of distillations, until after the eighteenth distillation it collected to the extent of 85 per cent. between 95° and 96°, under a constant tension of 730 mm., which for convenience was selected for all these distillations. In a large series of distillations a constant tension is simply and very conveniently obtained by means of the tension-regulator elsewhere described,[1] with the stopcock manipulated by a lever movable on a horizontal support. By a suitable adjustment of side tubes, stopcocks and adapters, any number of distillation-flasks may be introduced into the train, and regulated by the single stopcock. As many as fifteen distillations collecting in single-degree fractions have been in simultaneous operation with no interruption incident to changes of flasks or collection of distillates. It is quite impossible, in Cleveland, to carry on a course of distillations extending through several weeks without some form of tension-regulator, on account of sudden and extreme changes in the barometric pressure, occasionally equivalent to 25 mm. within a few hours.

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[1] Proc. Am. Acad., **31**, 24.

[2] J. Chem. Soc., 1865, p. 54.

Under 760 mm. and with the thermometer wholly in the vapor, chlorpentane distilled completely between 96° and 97°, for the most part at 96°.5. From a distillate below 30°, Pelouze and Cahours obtained a butyl chloride, as already mentioned, which boiled at 98°–103°.

The purity of our product is shown by analysis:

I. 0.1205 gram oil gave 0.2479 gram CO_2, and 0.1139 gram H_2O.

II. 0.2166 gram oil gave 0.2952 gram AgCl.

III. 0.2942 gram oil gave 0.4031 gram AgCl.

	Calculated for $C_5H_{11}Cl$.	Found. I.	II.	III.
C	56.33	56.13	....	....
H	10.43	10.51	....	....
Cl	33.33	....	33.69	33.88

A determination of the specific gravity of this chlorpentane at 20° gave 0.8750. Its vapor-density by the Hofmann method was found to have the following value:

0.1291 gram oil gave 72.6 cc. vapor at 100° under a tension of 384 mm.

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[1] Proc. Am. Acad., **31**, 10.

Calculated for $C_5H_{11}Cl$.	Found.
3.68	3.72

In forming isopentyl acetate, the purified chloride was heated 48 hours to 150°–160° with potassic acetate and glacial acetic acid. When washed, dried, and well fractioned, a small quantity collected at 134°–135° (760 mm.), which is somewhat lower than the boiling-point of isoamyl acetate, 138°.6. The amount of our material was not sufficient to raise its boiling-point, but it gave the required percentages of carbon and hydrogen.

0.1555 gram oil gave 0.3651 gram CO_2, and 0.1514 gram H_2O.

	Calculated for $C_5H_{11}C_2H_3O_2$.	Found.
C	64.60	64.00
H	10.80	10.81

When heated during several hours with alcoholic potash, the acetate was converted into the alcohol which was separated from the solution with salt. On account of the small quantity of alcohol obtained, its boiling-point could not be raised above 117°–120° (boiling-point of inactive amyl alcohol, 131°), although its composition corresponded to that of amyl alcohol.

0.1866 gram oil gave 0.4620 gram CO_2, and 0.2293 gram H_2O.

0.1854 gram oil gave 0.4610 gram CO_2, and 0.2315 gram H_2O.

	Calculated for $C_5H_{11}OH$.	Found.	
		I.	II.
C	68.18	67.51	67.81
H	13.63	13.66	13.88

At higher temperatures to 150°, the crude chlorine product could be distilled without decomposition. Above this point the residue was distilled *in vacuo*, which reduced its boiling-point to such an extent that further distillation could be carried on under atmospheric pressure, leaving only a very small residue above 150°, probably of substitution-products containing a large number of chlorine atoms.

At no point between 96° and 160° could a distillate be held constant, except at 144°–145°. Here five grams collected after the fifteenth distillation that distilled at 144°–146°, mostly at 145°, under 760 mm. and with the mercury column wholly in the vapor. This oil proved on analysis to have the composition required for dichlorpentane.

I. 0.1309 gram oil gave 0.2055 gram CO_2, and 0.0888 gram H_2O.

II. 0.1976 gram oil gave 0.3993 gram AgCl.

	Calculated for $C_5H_{10}Cl_2$.	Found. I.	Found. II.
C	42.56	42.84	....
H	7.09	7.54	....
Cl	50.36	....	49.96

A determination of the vapor-density of this body gave a value corresponding to dichlorpentane.

0.1680 gram oil gave 80.6 cc. vapor at 182° under a tension of 426 mm.

Calculated for $C_5H_{10}Cl_2$.	Found.
4.88	4.78

The boiling-point of this dichlorpentane is the same as that of amylene chloride, 145°, described by Bauer.[1] It is to be regretted that the quantity of our product was so limited; but on account of the great labor involved in its preparation, it did not seem advisable to attempt the preparation of a larger amount.

These results indicate that petroleum contains but one butane, and that is isobutane, which collects at 0°. That this body is not normal butane is shown by the boiling-point, 67°–68°, of the monochlor derivative, the boiling-point, 116°, of the acetate, that of the alcohol, 108°–109°, and that of the sulphide, 172°. It has hitherto been assumed that the butane in the petroleum is the normal hydrocarbon, because the butane prepared by Frankland from ethyl iodide and zinc boils at 0°. But isobutane prepared by Butlerow from tertiary butyl alcohol should boil at —17°.5. The differences between the properties of butane and isobutane are sufficiently marked to permit, without difficulty, of distinguishing between the isomeric forms.

Normal butyl chloride boils at 77°.6, and the alcohol at

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[1] Ztschr. Chem., 1866, 380.

117°. Since our series of derivatives from petroleum butane was prepared several times with the same results, and never with the formation of compounds with boiling-points corresponding to normal butane, there can be no question that normal butane is not contained in Pennsylvania nor in Ohio petroleum. The series question concerns the boiling-point of isobutane which we found in petroleum. As has been fully explained, our 0° fractions were separated as many as four different times from the lightest gasoline we could procure from the refinery. While we never failed to collect distillates below —10°, they were much smaller in quantity than those in the vicinity of 0°. It is, therefore, certain that the butane we had in hand was isobutane, and it seems equally certain that this hydrocarbon collected at 0° and not at —17°.

The Octanes in Ohio Petroleum.

It has already been pointed out by one of us[1] that the published accounts of the octanes in petroleum are not fully concordant. Pelouze and Cahours first announced in their series of hydrocarbons an octane, boiling-point 116°–118°, and a little later Schorlemmer[2] found a body in coal-tar distilling at 119°–122°, and another at 124°, both with the composition required for octane. Possibly led to believe by the results of Beilstein and Kurbatoff that the distillate 119°.5–122° is hexahydroisoxylol, in his latter summation of the octanes known, Schorlemmer seems to repudiate the one boiling at 119°–122°, which he had previously described. Warren recognized two octanes, one boiling at 119°.5, and another boiling at 127°.6. These bodies were identified alone by vapor-density determinations and boiling-points; no analyses were given. In the separation of the hydrocarbons resulting from the distillation under pressure of menhaden oil, Engler discovered the octane di-isobutyl, boiling-point 109°. In support of the work of Pelouze and Cahours, Lemoine[3] submitted American ligroïn to *four* fractional distillations, collecting distillates within limits of *five* degrees, and separated an octane, boiling-point 121° at 779 mm. In our experience, the hydrocarbons in petroleum with boiling-points not far removed can only be separated by the use of the best possible means for fractional separation, in a long course of distillations. The separation of the octanes, for example, requires a refinery distillate boiling between 120° and 170°, and it is not until the twentieth distillation that the octanes begin to accumulate with any degree of purity. In all our experiments after the fifth distillation, the octanes are still contained for the most part in the portions above 125°, and they are separated very slowly into their respective fractions. In undertaking further study of the octanes in Ohio petroleum, we procured from the refinery of Messrs. Schofield, Shirmer, and Teagle, 72 liters of a burning oil distillate that distilled in our hands, within the limit of ten degrees, in the following proportions :

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[1] C. F. M., *loc. cit.*

[2] J. Chem. Soc., **15**, 419.

[3] Bull. Soc. chim. (Paris), **41**, 161.

	—75°	75°–100°	100°–110°	110°–120°	120°-130°	130°-140°	140°-150	150°-160°	+160
Liters	10	12	10	8	8	8	5	5	5

The sulphur compounds were precipitated from these fractions by means of alcoholic mercuric chloride, the oils washed and dried, and the distillation continued within limits of 5°, 2°, and finally within 1°, under a constant tension of 730 mm. In further explanation of what was said above concerning the slow separation of these constituents, the following record of the tenth distillation is given ; when it is borne in mind that these weights are from 65 liters, the small amounts of the constituents will be appreciated :

	115°-116°	116°-117°	117°-118°	118°-119°	119°-120°	120°-121°	121°-122°
Grams	60	60	80	100	145	130	160

	122°-123°	123°-124°	124°-125°	125°-126°	126°-127°	127°-128°	128°-129°
Grams	120	170	160	150	120	90	40

If the distillation had been stopped at this point, since on account of the diminished tension the true boiling-points should be at least one degree higher than those given, it might be inferred that one of the principal constituents was a hydrocarbon boiling at 126°–127°.

No doubt this inference would be supported by the vapor-density of this product, but further distillation showed its fallacy. At the end of the thirty-third distillation, 190 grams collected at 118°.5–119°.5, which distilled between 119°.5–120°, for the most part at 119°.5, under 760 mm. with the mercury column wholly in the vapor. Its specific gravity at 20° was found to be 0.7243. This liquid was assumed to have the same composition as the octane whose identity was shown by analysis and a vapor-density determination.

The vapor-density of this product was found to support the same composition :

0.1287 gram oil gave 75 cc. vapor at 182°, under a tension of 429 mm.

Calculated for C_8H_{18}.	Found.
3.95	3.91

The specific gravity of the crude distillate was found to be 0.7256. The presence of this hydrocarbon is still furthur assured by the prolonged distillation. Our boiling-point is practically the same as that of Warren, although his product from Pennsylvania petroleum must have been contaminated to some extent by hexahydroisoxylol, which was not shown to be present in Pennsylvania oil until long after the work of Warren was completed. Our boiling-point was taken in a portion of the Ohio oil which had been subjected to prolonged treatment for the removal of hexahydroisoxylol. The specific gravity of this distillate purified by fuming sulphuric acid with the aid of heat was 0.7230. Another portion purified with a mixture of nitric and sulphuric acids, gave as its specific gravity 0.7190. In the oil with the same boiling-point separated from coal-tar, Schorlemmer found the specific gravity 0.7190 at 17°.5. In our product purified with fuming sulphuric acid, the required percentages of carbon and hydrogen were obtained :

0.1475 gram oil gave 0.4562 gram CO_2, and 0.2073 gram H_2O.

	Required for C_8H_{18}.	Found.
C	84.22	84.35
H	15.80	15.62

In the formation of chlorine derivatives from this octane, the same method was employed without cooling as in the case of the more volatile distillates. It was ascertained that the best yield of monochloroctane was given when the quantity of

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[1] Mabery: *Loc. cit.*

chlorine absorbed was 50 per cent. in excess of the amount theoretically required to form the monochlor derivative. Even with this excess, still a small amount of the hydrocarbon remained unchanged. Since it was found that the chlorinated compound could not be distilled under atmospheric pressure without serious decomposition, after washing and drying it was fractioned *in vacuo* under a tension of 50 mm., within limits of 10°, 5°, 2°, and finally for some time within 1°. Under 50 mm. fractions collected at all points between 65° and 150°, but a larger quantity at 83°-84°, which under atmospheric pressure, distilled at 164°-166°. The composition of this substance was determined by analysis:

I. 0.1479 gram oil gave 0.3523 gram CO_2, and 0.1537 gram H_2O.

II. 0.1961 gram oil gave 0.1888 gram AgCl.

III. 0.2483 gram oil gave 0.2408 gram AgCl.

	Calculated for $C_7H_{17}Cl$.	Found. I.	II.	III.
C	64.65	64.95	....	....
H	11.45	11.54	....	....
Cl	23.90	....	23.81	23.97

A determination of vapor-density gave a value required for monochloroctane:

0.1682 gram oil gave 78 cc. vapor at 182° under a tension of 400 mm.

Required for $C_8H_{17}Cl$.	Found.
5.14	5.28

The monochloroctane obtained by Pelouze and Cahours,[1] and by Schorlemmer,[2] from petroleum octane, boiling-point 168°-172°, was evidently a mixture of the two chloroctanes from the hydrocarbons 119°.5 and 124°. It could not be otherwise, on account of the imperfect separation of the hydrocarbons. In our experience, nothing less than thirty distillations is sufficient for the separation of these bodies with any degree of purity.

In comparing the results in this paper with those of others, it should be borne in mind that our products were separated from Trenton limestone petroleum, which was unknown at the time of the earlier study of Pennsylvania oil. But there can be little doubt that these portions of Pennsylvania and Ohio oils are identical so far as the principal constituents are concerned. That this is true of constituents with boiling-points above 150° will be shown in another paper.

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[1] Jsb. 1863, p. 528.

[2] Ann. Chem.. (Liebig), **125**, 112.

In many instances, even after the most careful purification, the specific gravity of the petroleum hydrocarbons is somewhat higher than that of the same hydrocarbons synthetically prepared. Schorlemmer[1] thought this was due to fine differences of isomerism. But this was before the discovery of naphtenes in petroleum. It now seems very probable that the higher specific gravity is due to the difficulty in removing the last trace of these bodies, especially since a small excess of carbon and a slight deficiency in hydrogen for the formula C_nH_{2n+2} accompanies the higher specific gravity. A notable quality of the naphtenes is their inertness toward reagents, which is doubtless greatly increased by large dilution in the principal petroleum hydrocarbons.

In Russian petroleum, Markownikoff[2] and Putochin discovered isoctonaphtene, boiling-point 122°.5. In looking for this hydrocarbon in Ohio petroleum the fractions 120°–124° were carefully distilled many times, until so little remained within these limits that no individual constituent could be present in any appreciable quantity, or in such quantity that it could be collected by fractional distillation and identified. The octane found by Lemoine at 121° is, therefore, also excluded.

The octane, boiling-point 125°.46, separated by Schorlemmer, was assumed to be identical with normal octane formed from normal butyl iodide by the action of sodium. Warren found a somewhat higher boiling-point for the octane from Pennsylvania petroleum. This body distilled between 126°.8 and 129°.1, or in the mean at 127°.6; its composition was based upon a determination of its vapor-density, but it was not supported by analysis. The observations of Warren were apparently confirmed by similar distillates separated from Ohio and Canadian petroleum.[3] Distillates collected at 126°–127° from these oils after the eleventh fraction gave values in vapor-density determinations corresponding to that of octane. But evidently such determinations, unsupported by other data, are less reliable, especially in products not far removed in boiling-points from other isomers. Although our former results apparently confirmed the presence of an octane at 129°–127°, those values were accepted as provisional, to be supported or modified by more prolonged distillations which have now been made.

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[1] Phil. Trans., **171**, 451, (1880).

[2] Ber. Chem. Ges., **18**, 1880.

[3] Mabery: Proc. Am. Acad., **31**, 32, 57.

Under a constant tension of 730 mm., forty-two distillations were made between 121° and 130° through Hempel bead columns. Of the last distillates scarcely any remained at 126°–127°, or between this point and 130°, and very little at 125°–126°. The greater portion, 200 grams, collected at 124°–125°, normal conditions. There is, therefore, in Ohio petroleum, no octane with a boiling-point higher than 125°. After purification with a mixture of nitric and sulphuric acids, and sodium, the distillate 124°–125° was shown by analysis to have the composition for octane :

0.1471 gram oil gave 0.4544 gram CO_2, and 0.2077 gram H_2O.

	Calculated for C_8H_{18}.	Found.
C	84.22	84.26
H	15.79	15.70

After thorough treatment with fuming sulphuric acid, this octane gave 0.7183 as its specific gravity. Another portion, carefully purified with a mixture of nitric and sulphuric acids gave 0.7134. The specific gravity of the synthetic hydrocarbon was given by Thorpe as 0.7188. The crude distillate, with no purification, gave as its specific gravity 0.7243. Its vapor-density was found by the method of Hofmann.

0.1578 gram oil gave 84.4 cc. vapor at 182°, under a tension of 462 mm.

Calculated for C_8H_{18}.	Found.
3.95	3.96

In the formation of monochloroctane from this distillate, the hydrocarbon was exposed to the action of chlorine in the cold until the increase in weight was fifty per cent. in excess of the quantity theoretically required to form monochloroctane. The product, containing a small amount of the hydrocarbon still unchanged, was washed, dried, and submitted to fractional distillation *in vacuo* under 50 mm., since it was found that it could not be distilled under atmospheric pressure without decomposition. A considerable portion collected at 89°–91°, that distilled under atmospheric pressure, normal conditions, at 173°–174°. Schorlemmer stated that chlorine converts normal octane into a mixture of primary octyl chloride, boiling-point 179°–180°, and secondary octyl chloride boiling at 175°. None of our product collected at the point corresponding to the normal chloride, although the quantity was not sufficient to determine the boiling-point with absolute precision, and not sufficient to form other compounds. Pelouze and Cahours[1] gave 168°–172° as the boiling-point of the chloride which they formed from petroleum octane, but their hydrocarbon was evidently not fully purified.

This substance gave upon analysis percentages of carbon, hydrogen, and chlorine required for chloroctane :

I. 0.1222 gram oil gave 0.2880 gram CO_2, and 0.1264 gram H_2O.

II. 0.1821 gram oil gave 0.1792 gram AgCl.

III. 0.2203 gram oil gave 0.2200 gram AgCl.

	Calculated for $C_8H_{17}Cl$.	Found. I.	II.	III.
C	64.65	64.27	....	....
H	11.45	11.19	....	....
Cl	23.90	....	24.33	24.69

A determination of vapor-density gave a value required for chloroctane :

0.1675 oil gave 76 cc. vapor at 182°, under a tension of 418 mm.

Calculated for $C_8H_{17}Cl$.	Found.
5.14	5.16

The small amount of distillates above 91° *in vacuo* showed the presence in minute proportions of higher chlorinated products, but it would require much larger quantities than we could conveniently procure to ascertain their composition.

Since Engler[2] discovered tetramethylbutane or diisobutyl, boiling point 108°.5, as one of the products in the distillation of fats under pressure, with the possibility that this body might be present in Ohio petroleum, we submitted the portions of this petroleum distilling between 100° and 115° to prolonged distillation within single-degree limits. But after treatment with nitric acid, no distillate collected in this vicinity. Having in hand a series of fractions near 135°–136°, the boiling-point of hexahydromesitylene, or nononaphtene, they were carried through a long course of distillations, and the small amount remaining within these limits was examined with the aid of fuming nitric acid and fuming sulphuric acid, but no sulphonic acid was formed, and the very small amount of nitro compound was not sufficient for a melting-point determination.

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[1] Jsb., 1863, p. 528.

[2] Ber. d. Chem. Ges., **22**, 592.

In view of the fact that the series of petroleum hydrocarbons boiling approximately at 38°, 68°, and 98°, has received little attention since it was first discovered by Warren, I shall soon undertake an examination of these bodies, and also of petroleum nonane to which Warren assigned the boiling-point 151°.

C. F. M.

Contributions from the Chemical Laboratory of Cornell University.

NAPHTHALENE TETRABROMIDE, $C_{10}H_8Br_4$.

BY W. R. ORNDORFF AND C. B. MOYER.

The chlorine addition-product of naphthalene, known as naphthalene tetrachloride, $C_{10}H_8Cl_4$, has been known for some time, having been prepared by Laurent[1] in 1833, and having since been studied by E. Fischer,[2] Leeds and Everhart,[3] Atterberg[4] and others.

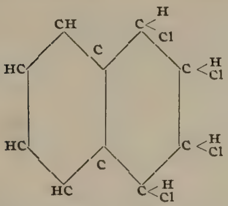
The corresponding tetrabromide, $C_{10}H_8Br_4$, has not yet been made, so far as we are aware. These two substances are exceedingly interesting from the standpoint of stereochemistry. Assuming that in naphthalene tetrachloride the halogen adds itself to only one of the benzene residues, an assumption that is proved to be correct by the fact that this tetrachloride yields only phthalic and oxalic acids on oxidation, we have the following structural formula for this substance :

[1] Ann. chim. phys. [2], **52**, 275 ; [2], **59**, 196.

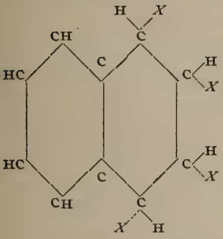
[2] Ber. d. chem. Ges., **11**, 735, 1411.

[3] J. Am. Chem. Soc., **2**, 205.

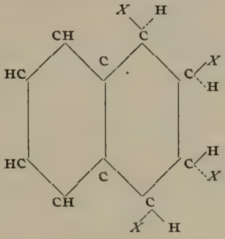
[4] Ber. d. chem. Ges., **11**, 1223.



Theoretically there should be three stereoisomers having this structural formula, as follows:



1.



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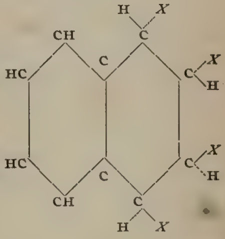

3.

In these formulas the dotted lines are intended to represent positions below the plane of the paper, while the unbroken lines represent those above this plane. Thus in formula 1 the halogen atoms, represented by the letter *X*, are all below the plane of the paper and the hydrogen atoms are above. This is the cis-form according to the nomenclature of von Baeyer. Formulas 2 and 3, both of which represent the trans-forms, are not identical, since they cannot be made to coincide, but represent enantiomorphous forms, and if they could be obtained in crystals, would probably be found to crystallize enantiomorphous.

These stereo-formulas are the only ones possible for the tetrahalogen addition-products of naphthalene where all the halogen atoms attach themselves to only one benzene ring.

Two naphthalene tetrachlorides have been described in the literature. The tetrachloride melting at 182° C. and formed by the action of chlorine on melted naphthalene has long been known. The other tetrachloride, generally called the β-compound to distinguish it from the α-product melting at 182° C., was first made by Laurent[1] in 1850, and afterwards by E. Fischer.[2] The latter obtained this compound together with the α-tetrachloride, by the action of potassium chlorate and hydrochloric acid on naphthalene. The two substances were separated by their difference in solubility in alcohol, the β-product being very soluble, while the α-product is only slightly soluble in this solvent. An analysis of the compound is given and the melting-point is stated to be 116°–118° C. It differed markedly from the α-tetrachloride in being very soluble in both alcohol and ether. During the same year, 1878, Atterberg published a short criticism of Fischer's paper, stating that he had made a special study of the action of chlorine on naphthalene and had sought in vain to isolate the β-naphthalene tetrachloride described by Fischer, and suggesting that the compound might have been dichlornaphthalene dichloride. Fischer, answering this article, adhered to his former opinion, and stated his intention to pursue the matter further at an early date; but up to the present he has published nothing further on this subject.

Naphthalene tetrachloride, made in several different ways, has been carefully examined by Mr. D. A. Morton, one of the advanced students in this laboratory, in order to see if it could be obtained in more than one form. It was not found possible, however, to make an addition-product differing in any way from the α-product melting at 182° C., nor could this product be separated into two substances by any of the methods made use of. An oily product was obtained in the preparation of the tetrachloride by the method given by E. Fischer, which gave off hydrochloric acid when heated; but whether this was a new tetrachloride or only a monochlornaphthalene containing some dissolved naphthalene tetrachloride or naphthalene dichloride could not be determined.

Three tetrabromides of α-nitronaphthalene as well as two dibromnaphthalene tetrabromides have been prepared by Guareschi,[3] and as it seemed highly probable that naphthalene itself would yield addition-products with bromine, the following investigation was undertaken to see if naphthalene tetrabromide could be made, and if so, whether it existed in more than one stereochemical modification. The preliminary part of this work was done by Dr. F. K. Cameron, now of the Catholic University of Washington, who not only found that naphthalene tetrabromide could be made by the addition of bromine to naphthalene, but also succeeded in isolating a small quantity of the product and identifying it by a determination of the amount of bromine it contained.

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[1] Compt. rend. des Travaux de chimie, 1850, 1: Ann. Chem. (Liebig), **76**, 298.

[2] Ber. d. chem. Ges., **11**, 735.

[3] Ann. Chem. (Liebig), **222**, 285; Gaz. chim. ital., **16**, 142.

Method of Preparation of Naphthalene Tetrabromide.

The method used in preparing the naphthalene tetrabromide was as follows: 100 grams of finely powdered *pure* naphthalene were placed in an Erlenmeyer flask, together with some cracked ice and a small quantity (200 cc.) of a 4 per cent. solution of sodium hydroxide. The flask was then surrounded with ice water and 150 grams of bromine were run in slowly from a dropping-funnel,[1] the lower end of which was drawn out to a very narrow opening, and which dipped below the surface of the liquid in the flask. The flask was shaken constantly during the addition of the bromine, and the ice in the flask replaced by a fresh supply as it melted. Little or no hydrobromic acid was given off under these conditions and complete addition of the bromine to the naphthalene seemed to have taken place, a deep-red, pasty mass resulting. The flask and its contents were allowed to stand in a cool place for a few hours—generally over night. The water was then decanted from the pasty mass, which was afterwards ground up and thoroughly washed with cold water. It was then treated repeatedly with small quantities of luke-warm alcohol, which extracted the unchanged naphthalene, the α-monobromnaphthalene and the 1-4 dibromnaphthalene. After repeated extractions in this manner, a small quantity of a white solid was obtained, which was but slightly soluble in alcohol and which melted at 116°–120° C. This was then recrystallized several times from chloroform, yielding a transparent, colorless, well crystallized product, melting at 111° C. The yield was about seven grams.

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[1] The bromine in the dropping-funnel was kept covered with ice water to prevent evaporation and also to keep the bromine cold.

A determination of the amount of bromine in this purified product by the Carius method gave the following results:[1]

I. 0.1780 gram of the substance gave 0.3031 gram of AgBr.

II. 0.2173 gram of the substance gave 0.3662 gram of AgBr.

	Calculated for $C_{10}H_8Br_4$.	Found.	
		I.	II.
Bromine	71.42	72.47	71.69

The results obtained by Dr. Cameron with the product isolated by him were as follows:

0.2634 gram substance gave 0.4443 gram AgBr.

	Calculated for $C_{10}H_8Br_4$.	Found.
Bromine	71.42	71.67

As the product was made from naphthalene by the addition of bromine and was undoubtedly a tetrabrom addition-product, it was not thought necessary to determine the amounts of carbon and hydrogen it contained.

The heavy oily portions extracted by the warm alcohol were put together, and, after most of the solid matter had been crystallized out by cooling in a freezing-mixture, the alcohol was evaporated and the residue subjected to distillation in superheated steam. The first substance to distil was unchanged naphthalene, then α-monobromnaphthalene and finally 1 : 4 dibromnaphthalene. On redistilling the oily α-bromnaphthalene alone it bumped violently and gave off both bromine and hydrobromic acid, indicating the presence of an addition-product; but whether this was due to some of the solid naphthalene tetrabromide being dissolved in the oily bromnaphthalene, or to an oily tetrabromide or to a dibrom addition-product, could not be ascertained, as it was not found possible to isolate any pure substance from the product save the α-monobromnaphthalene.

Numerous modifications of the method were tried with a view of increasing the yield of the tetrabromide, but in none of these was the yield increased, nor could any other tetrabromide be isolated.

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[1] In calculating these results we used the following atomic weights: Ag, 107.92; Br, 79.95; C, 12.01; H, 1.008, taken from Clarke's Constants of Nature, 1897.

Properties of the Naphthalene Tetrabromide.

The tetrabromide made by the above method is a solid melting at 111° C., with decomposition, giving off bromine and hydrobromic acid. It is insoluble in water, ether, glacial acetic acid and cold alcohol; very slightly soluble in hot alcohol, and readily soluble in carbon disulphide, ligroïn, hot chloroform, and hot benzene. It crystallizes in transparent monoclinic prisms, which become opaque on standing in the light, or when heated, this opaqueness probably being due to surface evaporation from the crystals. When kept in the dark and in a tolerably cold room they preserve their transparency and brilliancy for some time; but eventually become opaque and assume a red color from the separation of the bromine.

A large number of the crystals carefully recrystallized from chloroform were examined by Professor A. C. Gill, of the Mineralogical Department of this University, to whom we are much indebted for the following report:

"The brilliant, colorless crystals of naphthalene tetrabromide are very variable in shape, usually flattened parallel to a prism face. From measurements on about fifteen crystals, most of which were one to two mm. in diameter, the crystal system was determined to be monoclinic, with the following angles and axial ratios:

$\beta = 67° 3'$ à : b̄ : ċ = 1.2075 : 1 : 1.4775.

Angles.	Calculated.	Found.	Number of observations.
$001 : 110$		74° 53′	11
$001 : \bar{1}01$		65° 06′ 30″	14
$\bar{1}01 : \bar{1}11$		47° 36′ 30″	6
$110 : 1\bar{1}0$	96° 04′	96° 02′	10
$001 : 101$	37° 20′	37° 21′ 40″	6
$001 : 011$	53° 41′	53° 38′	2
$\bar{1}11 : \bar{1}\bar{1}0$	31° 36′	31° 37′	7
$001 : \bar{1}11$	73° 31′	73° 30′	12
$\bar{1}11 : 011$	40° 15′ 30″	40° 23′	1

Of the six forms included in this list, the prism, 110; the base, 001; and the positive orthodome, 101, are usually the principal faces of the crystals. The other three forms occur as modifications on the edges and angles.

The accompanying figures show two of the most common shapes of the crystals.

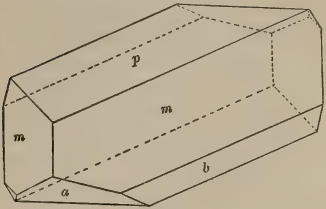

Fig. 1.

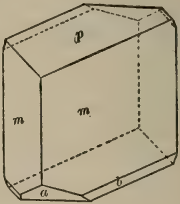

Fig. 2.

$p = (001)$, $m = (110)$, $a = (10\bar{1})$, and $b = (11\bar{1})$.

The question whether the tetrabromide of naphthalene is isomorphous with the tetrachloride must be looked upon as undecided. There is a close resemblance between the angle β of the two substances; for the former it is 67° 3′, and for the latter 67° 19′. But in order to show further likeness in the crystallographic elements, it is necessary to assume that the prevailing parameter on the vertical axis of the tetrabromide is $\frac{3}{2}$, and,on the clinoaxis is 2. This rather forcible assumption would give:

$\grave{a} : \bar{b} : \acute{c}$

0.8050 : 1 : 0.7388 for the tetrabromide,

and 0.7715 : 1 : 0.6921 for the tetrachloride.

This is after all not a very close agreement."

A very small quantity of the dibromnaphthalene existing in the tetrabromide will cause the crystals of the latter to become elongated along one edge. These elongated crystals were at first thought to be a second tetrabromide, but on examination by Dr. Gill, they were found to be identical with the other crystals.

Many attempts were made to separate from this tetrabromide a stereoisomer by using various solvents, some of which were optically active, but without success.

When the tetrabromide was heated in a test-tube several degrees above its melting-point, in a sulphuric acid bath, bromine and hydrobromic acid were given off, the resulting product being a red oil. This oil was soluble in cold alcohol and on evaporation a small portion of a solid, which proved to be 1-4 dibromnaphthalene, came down first, and then a light yellow oil, which was identified as the α-monobromnaphthalene.

When the tetrabromide is boiled with an alcoholic solution of potassium hydroxide for a couple of hours it is completely decomposed. The product consists mainly of an oil which was identified as α-bromnaphthalene.

On oxidation with nitric acid the only product that could be identified was phthalic acid.

Two attempts were made to determine the molecular weight of the naphthalene tetrabromide, using the boiling-point method and chloroform and carbon disulphide as solvents; but even in these low-boiling solvents decomposition takes place, both hydrobromic acid and bromine being evolved. The first pellet introduced into the boiling liquid in both cases produced a fall instead of a rise of temperature, so that the results were valueless. It was then thought that the molecular weight of the tetrabromide might be deduced from the molecular weight of the naphthalene tetrachloride. In making all these molecular weight determinations the boiling-point apparatus devised by Orndorff and Cameron[1] was used.

A determination of the molecular weight of some of the pure naphthalene tetrachloride made by Mr. D. A. Morton, gave the following results:

Naphthalene Tetrachloride, $C_{10}H_8Cl_4 = 270$.

Solvent: Chloroform. Boiling-point 60°.2 C. at 741.7 mm. Molecular elevation for 100 grams 36°.6.

Grams solvent.	Grams substance.	Concentration in 100 grams.	Rise observed.	Molecular weight.
186.77	0.6008	0.3108	0.040°	284.5
	1.2548	0.6718	0.079	311.2
	1.8890	1.0114	0.110	336.5
	2.4779	1.3267	0.140	346.8
	3.0584	1.6375	0.179	334.8
Molecular weight at infinite dilution				276

Barometer constant.

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[1] This JOURNAL, 17, 517.

Grams solvent.	Grams substance.	Concentration in 100 grams.	Rise observed.	Molecular weight.
202.22	0.6041	0.2987	0.052°	210.2
	1.1597	0.5735	0.090	233.2
	1.8410	0.9104	0.130	256.3
	2.4701	1.2215	0.170	262.9
	3.1011	1.5335	0.220	255.1

Molecular weight at infinite dilution	208

Barometer constant.

The erratic results in these determinations of the molecular weight of the tetrachloride are caused by a slight decomposition of the tetrachloride, as shown by the evolution of hydrochloric acid during the determinations, and by the difference in the melting-point of the substance before and after the determinations. The tetrachloride before being used melted sharply at 180° C., and after the experiment at 165°–169° C.

The results show clearly, however, that the molecular weight of the tetrachloride is approximately 270, and that the formula of the substance is $C_{10}H_8Cl_4$, and in all probability that the formula of the tetrabromide is $C_{10}H_8Br_4$.

Regarding the stereochemical formulas of the naphthalene tetrachloride and tetrabromide, it seems quite likely from the fact that they both crystallize in the monoclinic system, that the space formula which best represents the position of the atoms in both substances, is either formula 2 or 3 given above, or they may be a mixture of both substances represented by these formulas, since it would be impossible to separate a mixture of this sort by any method now known to us.

Further work on the chlorine and bromine addition-products of naphthalene and its derivatives is already under way in this laboratory.

CORNELL UNIVERSITY,
FEBRUARY, 1897.

Contributions from the Chemical Laboratory of Harvard College.

XCVIII. — ON HYDROCOBALTOCOBALTICYANIC ACID AND ITS SALTS.

By C. Loring Jackson and A. M. Comey.

The work described in this paper was undertaken in the hope of preparing, from potassic cobalticyanide, compounds analogous to the nitroprussides. The prospect of obtaining this result was not very good, as the only previous statement about the action of nitric acid on potassic cobalticyanide was that of Zwenger,[1] who says: "Beim Kochen (of hydrocobalticyanic acid) mit Salpetersäure tritt gleichfalls keine Zersetzung ein, und man kann sie selbst auffallender Weise mit rauchender Salpetersäure anhaltend erhitzen ohne dass dadurch eine Zerstörung erfolgt." Nevertheless, it seemed to us worth while to repeat the experiment. Accordingly, we boiled about 75 to 100 cc. of a strong solution of potassic cobalticyanide with its own volume of common strong nitric acid in an open flask. At first it seemed as if Zwenger's statement was correct, as the mixture underwent no apparent change during the first three minutes, but in less than five minutes the liquid turned red, and this color increased in intensity as the boiling was continued. After boiling for about two hours the dark red solution was suddenly converted into a semi-solid gelatinous mass. On one occasion, when the quantity of solution was larger than usual, and the heat was not moderated soon enough, the reaction was so violent as to throw a large part of the gelatinous substance out of the flask in which the process was carried on. This red gelatinous product was purified by heating it with a little more nitric acid on the water-bath, and, after breaking up the lumps as thoroughly as possible, washing it with a large amount of water. As the impurities were removed the substance began slowly to go into solution, and this generally indicated that it was pure; but, if it was necessary to wash it longer, this could be done by evaporating the moist precipitate to dryness on the water-bath, which rendered it insoluble again. It was found in the preparation of the substance that essentially all the cobalt had remained in the precipitate, the first filtrate containing only nitric acid, potassic nitrate, and hydrocyanic acid. The insoluble jelly was dried *in vacuo* for analysis, when it changed from red to a grayish-green color, but this dried salt is very hygroscopic, absorbing water rapidly from the air and regaining its red color. In fact it is so sensitive to moisture that it could be used as a very delicate test for the presence of aqueous vapor.

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[1] Ann. Chem. (Liebig), 62, 161.

In analyzing the substance we first made a combustion of it in an open tube. This gave us the carbon, and also the amount of water, which we did not dare to determine by loss, as there was danger of a loss of hydrocyanic acid at the same time. As the substance contained potassium, a portion of the carbonic dioxide remained in the residue as potassic carbonate. To determine this the contents of the boat were transferred to a flask, and heated with dilute sulphuric acid, the carbonic dioxide set free, being swept out by a stream of dry air through a drying tube and the absorption bulbs. The solution of cobaltous sulphate and potassic sulphate left in the flask was then worked up with ammonic sulphide in the usual way, and the two metals weighed as sulphates. This method gave excellent results because the substance burnt quietly without any spirting, so that the whole of the inorganic matter was left in the boat.

Each of the following analyses was made with an entirely different preparation:

I. 0.2536 gram of the salt gave 0.2346 gram of carbonic dioxide and 0.0200 gram of water. Also 0.2281 gram of cobaltous sulphate. The potassic sulphate was not determined.

II. 0.2458 gram of the salt gave 0.2272 gram of carbonic dioxide, 0.0178 gram of water, and 0.0400 gram of potassic sulphate.

III. 0.2496 gram of the salt[1] gave, when evaporated with sulphuric acid, 0.2245 gram of cobaltous sulphate and 0.0408 gram of potassic sulphate.

IV. 0.2403 gram of the salt[1] gave 0.2143 gram of cobaltous sulphate and 0.400 gram of potassic sulphate.

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[1] In these two analyses the amount of water was determined by the loss on heating. The percentages obtained were 0.97 and 1.05, both of which are somewhat too high because hydrocyanic acid was also given off, as was shown by the smell.

	Calculated for $KH_2Co_3(CN)_{11}H_2O$.	Found.			
		I.	II.	III.	IV.
Carbon	25.28	25.24	25.21	....	....
Hydrogen	0.77	0.88	0.80	....	....
Cobalt	33.90	34.24	....	34.24	33.94
Potassium	7.49	....	7.31	7.34	7.47

These analyses establish the composition of this salt and are confirmed by those of the other salts given later in this paper. We have assigned provisionally to the acid, $H_3Co_3(CN)_{11}$, from which this salt is derived, the name hydrocobaltocobalticyanic acid. This salt therefore is the monopotassic cobaltocobalticyanide.

Properties of Monopotassic Cobaltocobalticyanide, $KH_2Co_3(CN)_{11}H_2O$.—This substance, as first obtained in the moist state, appears as a red jelly a little duller in tint than currant jelly. When its solution is evaporated to dryness on the water-bath, it forms a reddish-brown mass looking like shellac, which by the action of water is converted into a brownish red powder. When dried *in vacuo*, or at 100°, it becomes grayish-green, but takes up water with great avidity, regaining its red color. Its behavior toward water is peculiar. The crude product is insoluble in cold water and nearly so in hot, but, after the impurities have been washed out, it usually dissolves slowly and to a limited extent in cold water, although its behavior varies in different specimens; thus, one after standing with cold water for two weeks imparted a slight red color to the liquid, while another, which stood for two months, did not color it at all. On the other hand, digestion with a small amount of water at 60° brings it completely into solution. The speed, with which this solution takes place, depends on the treatment the gelatinous substance has received; if it had been allowed to remain for some time suspended in water, it dissolved very slowly, taking several days for complete solution; if it had been filtered out and dried, it began to dissolve in a very few minutes; yet even in this case it took from twelve to forty-eight hours to dissolve 2 grams completely. The dark-red solution thus obtained can be concentrated without depositing any of the salt; in fact this only begins to appear as the solution runs to dryness. If the residue, which looks like shellac, is covered with cold water, it decrepitates with a series of insignificant explosions to a red powder, which is essentially insoluble in cold water, so that it can be washed with a large amount of it without perceptible loss; but, if it is digested with a small amount of water at 60°, it gradually dissolves, forming a solution in all respects like that obtained from the original product. The solution has a strong acid reaction, and gives precipitates with the salts of many of the metals as follows:

With a salt of barium, calcium, zinc, or manganese, a salmon-colored precipitate.

With ferric chloride, a yellowish-brown precipitate.

With ferrous sulphate, light-yellow.

With a salt of nickel, grayish-yellow.

With a salt of cobalt, flesh color.

With a salt of copper, greenish-blue.

With a salt of silver, salmon-colored.

With a salt of lead, a slight yellow precipitate.

With a salt of magnesium or mercury, no precipitate.

The aqueous solution was not precipitated by alcohol alone, but if a salt of potassium was also added, the dipotassic salt was precipitated.

Dipotassic Cobaltocobalticyanide, $K_2HCo_3(CN)_{11}.2H_2O$.—This salt was made by mixing a solution of the monopotassic salt and potassic acetate and then adding enough alcohol to precipitate it. The salt appeared as a pink, flocculent precipitate, which dissolved in cold water only after long standing, but quickly and easily in hot water. It is insoluble in alcohol. For analysis it was dried *in vacuo*:

0.2240 gram of the salt gave 0.1770 gram of cobaltous sulphate and 0.0684 gram of potassic sulphate.

	Calculated for $K_2HCo_3(CN)_{11}.2H_2O$.	Found.
Cobalt	30.61	30.08
Potassium	13.52	13.72

We have not yet succeeded in preparing the tripotassic salt, but think this might be done after a more careful study of the conditions of its formation.

An especially careful study of the barium and the silver salt was made in order to establish more firmly the composition of this series of compounds.

Baric Cobaltocobalticyanide, $BaHCo_3(CN)_{11}.1\frac{1}{2}H_2O$.—This salt was made by adding an excess of baric nitrate or chloride to the solution of the monopotassic salt. The precipitate, which is soluble in an excess of the potassium salt, was purified by washing with water, dried at 180°, and analyzed with the following results:

I. 0.2698 gram of the salt gave on combustion 0.2024 gram of carbonic dioxide, 0.0156 gram of water, 0.2004 gram of cobaltous sulphate, and 0.0997 gram of baric sulphate.

II. 0.3027 gram of the salt gave 0.2294 gram of cobaltous sulphate and 0.1134 gram of baric sulphate.

	Calculated for	Found.	
	$BaHCo_3(CN)_{11}.1\frac{1}{2}H_2O$.	I.	II.
Carbon	21.02	20.46	....
Hydrogen	0.64	0.64	....
Cobalt	28.18	28.23	28.19
Barium	21.82	21.72	21.82

It is a striking fact that this salt retains the 1.5 molecules of water of crystallization even at the high temperature of 180°. Its behavior, when heated, was peculiar. At 100° it turned slate color, at 180° it was a dull slate blue, and at 225° it took on a pure, clear blue color. It was evident, however, that the salt was decomposed at 225°, since on exposure to the air the blue substance turned to a pale, reddish-brown, distinctly different from the salmon color of the original salt, and when it was treated with water a gas was given off with an odor similar to that of hydrocyanic acid, but not identical with it, whereas the barium salt is not decomposed by water. This decomposition of the barium salt at 225° was accompanied by a slow but long-continued loss of weight.

The barium salt, when washed free from impurities, dissolved in water, but, when obtained by the evaporation of its solution to dryness on the water-bath, it became insoluble even in hot water.

Argentic Cobaltocobalticyanide, $Ag_3Co_3(CN)_{11}.H_2O$.—This salt was made by adding a large excess of argentic nitrate to the solution of the monopotassic salt. It was a salmon colored precipitate, which was purified by washing with water. It was dried *in vacuo* for analysis:

I. 0.2254 gram of the salt gave 0.1392 gram of carbonic dioxide, 0.0084 gram of water, 0.1309 gram of cobaltous sulphate, 0.1154 gram of argentic chloride, and 0.0020 gram of silver.

II. 0.3094 gram of the salt gave 0.1910 gram of carbonic dioxide, 0.0082 gram of water, 0.1774 gram of cobaltous sulphate, 0.1624 gram of argentic chloride, and 0.0012 gram of silver.

	Calculated for $Ag_3Co_3(CN)_{11}.H_2O$.	Found.	
		I.	II.
Carbon	16.40	16.84	16.83
Water	0.25	0.41	0.30
Cobalt	21.99	22.09	21.82
Silver	40.24	39.73	39.89

The silver salt is a salmon colored, flocculent precipitate, which turns brick-red when dried in the air, and becomes slate green *in vacuo*; but like all the other salts of this acid it takes up water again with the utmost ease, even a few seconds exposure to the air being enough to restore its red color.

Cupric Cobaltocobalticyanide, $Cu_3[Co_3(CN)_{11}]_2.4H_2O$.—This salt was made by precipitating a solution of the monopotassic salt with cupric sulphate. The greenish-blue, flocculent precipitate was washed thoroughly with water and then dried *in vacuo*. When dry and pulverized it formed a bright, emerald green powder.

0.2534 gram of the salt, dried *in vacuo*, gave 0.2080 gram of carbonic dioxide, 0.0246 gram of water, 0.1950 gram of cobaltous sulphate, and 0.0412 gram of copper.

	Calculated for $Cu_3[Co_3(CN)_{11}]_2.4H_2O$.	Found.
Carbon	22.22	22.39
Hydrogen	0.67	1.08
Cobalt	29.80	29.29
Copper	16.01	16.26

Zincic Cobaltocobalticyanide, $ZnHCo_3(CN)_{11}.3H_2O$.—This salt was made by adding to an alcoholic solution of the monopotassic salt an aqueous solution of zincic chloride; a salmon-pink precipitate was thrown down which was washed with alcohol. This substance was analyzed with the results given under I. In a second experiment aqueous solutions were used and an exactly similar result was obtained, the analysis of which is given under II. For the first analysis the salt was dried at 100°, when it took on a grayish color; for the second it was dried *in vacuo*.

I. 0.3540 gram of the substance gave 0.2923 gram of carbonic dioxide, 0.0442 gram of water, and 0.0470 gram of zincic oxide.

II. 0.3865 gram of the substance gave 0.3253 gram of carbonic dioxide and 0.0374 gram of water.

	Calculated for $ZnHCo_3(CN)_{11}.3H_2O$.	Found.	
		I.	II.
Carbon	22.64	22.52	22.94
Hydrogen	1.20	1.39	1.08
Zinc	11.15	10.65	....

The analysis of these salts prove conclusively that the acid is tribasic.

The free hydrocobaltocobalticyanic acid was obtained by treating hydrocobalticyanic acid with nitric acid precisely as was done with the potassic cobalticyanide in making the monopotassium salt. It resembles this salt most closely in its red color, gelatinous consistency, and solubility, but, is less stable, as it gives off hydrocyanic acid when dried. On this account we did not attempt to analyze it.

Action of Potassic Hydrate on Monopotassic Cobaltocobalticyanide.

When an excess of potassic hydrate was added to a solution of the monopotassic cobaltocobalticyanide, it turned dark-brown in the cold, and, if the liquid was warmed, this color deepened to a black, but nothing was precipitated until the solution was boiled, when after a few minutes a black precipitate of cobaltic hydrate was formed. The separation of this cobaltic hydrate is slow and gradual. It required from twenty-four to thirty-six hours to remove the whole of it. Before it is complete, if the precipitate was filtered out, a yellowish solution was obtained, from which renewed boiling separated more of the cobaltic hydrate. After no more cobaltic hydrate was formed the liquid was filtered and the light-yellow filtrate acidified with acetic acid, when no odor of hydrocyanic acid was observed. Alcohol was then added, which precipitated fine yellow or white needles, the excess of potassic hydrate, which had been converted into potassic acetate, remaining in solution. The precipitate was dissolved in a little water and then treated with an amount of alcohol insufficient for complete precipitation. This threw down a yellow oil, which was filtered out and the addition of an excess of alcohol to the filtrate gave a precipitate of white needles. The needles were purified by crystallization from water three times, and then analyzed with the following results:

I. 0.1620 gram of the substance, dried *in vacuo*, gave on combustion 0.1286 gram of carbonic dioxide.[1]

II. 0.3094 gram of the substance, dried at 100°, gave 0.1450 gram of cobaltous sulphate and 0.2438 gram of potassic sulphate.

	Calculated for $K_6Co_2(CN)_{12}$.	Found. I.	II.
Carbon	21.67	21.65	....
Cobalt	17.75	....	17.84
Potassium	35.30	....	35.37

The substance is therefore, according to this analysis, potassic cobalticyanide, but we found it hard to believe this was the case, because it crystallized, as already stated, in little needles most unlike the characteristic broad, rhombic crystals of the potassic cobalticyanide, and we could not, even by numerous crystallizations, succeed in making it crystallize in the usual form. We decided, therefore, that some confirmatory work was necessary before we admitted that this substance was potassic cobalticyanide, and for this purpose converted it into the sodium salt, which crystallizes with water. The potassium salt was first converted into the copper salt, and this by sulphuretted hydrogen into the free acid. The copper salt had the color of the cobalticyanide and the acid crystallized in long silky needles exactly resembling those derived from a sample of ordinary potassic cobalticyanide, but on neutralizing a little of each of these preparations with potassic hydrate, the one from our salt gave needles, that from the ordinary cobalticyanide rhombic crystals as before. The main portion of each sample of acid was converted into the sodium salt by neutralization with sodic hydrate, each sample dried *in vacuo*, and the water of crystallization determined with the following results :

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[1] In the combustion 0.0050 gram of water were found amounting to 0.34 per cent. It was undoubtedly hygroscopic.

I. 0.3644 gram of the sodium salt prepared from the needle-formed potassium salt, lost 0.0442 gram when dried at 100°.

II. 0.5342 gram of the sodium salt prepared from potassic cobalticyanide lost 0.0626 gram when dried at 100°.

	Calculated for $Na_6Co_2(CN)_{12}.4H_2O$.	Found. I.	II.
Water	11.25	12.13	11.71

There can be no doubt therefore that the substance obtained by us through the action of potassic hydrate on potassic cobaltocobalticyanide is potassic cobalticyanide. We are inclined to think that the unusual crystalline form, in which it appeared, was due to the presence of a small amount of impurity, probably the oily product of the reaction already mentioned, although the analyses show that the needles were nearly pure potassic cobalticyanide, and in some experiments we found that it was necessary to add a very large amount of this oily impurity to potassic cobalticyanide to make it crystallize in needles ; in fact the needles began to appear only when so much of the mixture of oil and our needle-formed cobalticyanide had been added, that they might have consisted of this, crystallizing out.

The secondary product, which was precipitated as an oil, was converted into a very deliquescent yellow solid by drying at 100°. We have not yet succeeded in finding a method of purifying it, but hope that some experiments now in progress may bring it into a state fit for analysis. When the triargentic cobaltocobalticyanide was treated with sulphuretted hydrogen, what seemed to be a new compound was formed, which will be investigated in this laboratory.

Conclusion.

Many of the peculiar properties of the substances described in this paper also appear in the ferrocyanides and ferricyanides. Thus Prussian blue is a colloid substance like our monopotassium salt, and the obstinacy with which our salts retain their water (the silver salt at 130°, the barium salt even at 180°), recalls the fact that Prussian blue dried at 100° contains, according to Carius and Reimann,[1] 12 molecules of water, and even when heated to 160°, according to Rammelsberg,[2] 9 molecules, which are not given off till 250°. The solubility of the monopotassium salt also is like that of soluble Prussian blue up to a certain point, since both are insoluble as at first formed, but become soluble when the impurities are washed out, and are rendered insoluble in cold water by drying at 100°, but we cannot find that the soluble Prussian blue shows the property of dissolving again in warm water, after it has been rendered insoluble in cold, which is so characteristic of our monopotassium salt.

This analogy between soluble Prussian blue and our monopotassium salt might lead to the supposition that they were similarly constituted, in other words that one of the atoms of cobalt in our compounds is in the basic part of the salt, but, if this were so, potassic hydrate should give a precipitate of cobaltous hydrate in the cold, and it does not. A precipitate is formed, to be sure, on boiling our monopotassium salt with potassic hydrate, but it is cobaltic hydrate, and is attended by a complete decomposition of our compound into potassic cobalticyanide and the salt of some other, as yet unrecognized acid. Further, on this supposition, the atom of basic cobalt should be replaced by two of silver, when the monopotassium salt is treated with argentic nitrate, but this is not the case, as the salt $KH_2Co_3(CN)_{11}$ gives under these conditions the triargentic salt $Ag_3Co_3(CN)_{11}$. We must infer, therefore, that all of the cobalt in our salts is in the acid part of the molecule.

None of the compounds of iron and cyanogen seem to be constituted like our salts, so that we cannot help ourselves by analogy in speculations on the nature of these salts. In the absence of definite knowledge in regard to their constitution we have thought it wise to rest on the fact that the formula $H_3Co_3(CN)_{11}$ amounts to 3 molecules of hydrocyanic acid combined with one of cobaltocobalticyanide, thus $(HCN)_3Co_3(CN)_6$, and therefore to give these substances the provisional name of cobaltocobalticyanides.

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[1] Ann. Chem. (Liebig), **113**, 41.

[2] Pogg. Ann., **73**, 80.

We hope that the work will soon be extended in this laboratory to compounds analogous to the cobalticyanide. We have tried already some preliminary experiments on potassic ferricyanide, which was converted by boiling with nitric acid into a black jelly having similar properties to the red gelatinous monopotassic cobaltocobalticyanide, and drying to a jet black varnish. As it seemed less stable than the corresponding cobalt compound, we have postponed its study, until we have mastered that substance. Its black color recalls that of potassic perferricyanide, but it seems to be still more closely related to the black compound, $Fe_3(CN)_8$, which Edgar Reynolds[1] obtained by the action of bromine on potassic ferricyanide.

ON THE ANALOGIES IN COMPOSITION OF THE SALTS OF CALCIUM, STRONTIUM AND BARIUM.

By J. H. Kastle.

That certain analogies in the composition of calcium, strontium and barium salts, anhydrous and hydrated, exist has, of course, been recognized for a long time. In fact the resemblance in composition between the chlorides, nitrates, sulphates, etc., of these elements is nearly always cited as one of the strongest arguments in favor of the family relationship of these metals.

To what extent such analogies exist has, so far as I can discover, never been made out. It is true that along this line a great many attempts have been made to trace resemblances and find relationships existing between the hydrated salts of related acids and metals.

Important contributions to our knowledge of this subject have been made by Salzer,[1] whose rules concerning water of crystallization are doubtless familiar to the majority of chemists. His work has, however, no immediate bearing upon the problem in hand, and hence will not be discussed. In fact the only work bearing immediately upon the subject under consideration is that of Lenssen.[2] As the result of his work on triads of related elements, this observer was led to conceive of a more intimate relation existing between two of the elements composing the triad than was supposed to exist between those composing the triad itself. In other words, he assumed the existence of a dyad within the triad. Among the other facts which he cited in support of his conclusion were the relationships existing between the amounts of water of crystallization of the salts of the two metals composing the dyad, and concerning which he laid down the following rules :

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[1] J. Chem. Soc. (London), **53**, 767 (1888).

The salts which an acid forms with members of a dyad contain :

1. Equal numbers of molecules of water of crystallization, or are anhydrous respectively, or

2. That salt contains the greater number of molecules of water of crystallization whose base has the smaller equivalent in the dyad.

According to him calcium, strontium and barium form a triad in which the dyad relation is exhibited by strontium and barium ; and in support of his theory he cited the composition of the strontium and barium salts of 30 acids ; and, in the case of strontium and barium salts, he reached the further conclusion that the salts of these two metals either contain the same number of molecules of water of crystallization or the strontium salts contain 4 more than those of barium.

Without entering into a detailed criticism of Lenssen's conclusion, it may be observed that while the relations of elements as implied in the triad are still about the closest of those exhibited in the natural family, it would seem that the necessity for the still further and inner relation of the dyad within the triad itself has never made itself felt. It is, further, to be borne in mind that many valuable contributions to our knowledge of the chemistry of the salts of metals and acids have been made since this time (1857), and that the data now at hand are vastly greater than they were then.

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[1] Ann. Chem. (Liebig), **223**, 1.

[2] *Ibid*, **103**, 121.

It was deemed advisable, therefore, to institute this comparison as to the composition of calcium, strontium and barium salts, anhydrous and hydrated,[1] and it will be seen that the analogies existing in the composition of the salts of these metals are deeper and more comprehensive than those included in Lenssen's rules.

The following standard works of reference were used in making this comparison: Watts' Dictionary of Chemistry, (Morley and Muir); Beilstein's Handbuch der organischen Chemie; Comey's Dictionary of Solubilities. The examination showed that 141 acids have been described, whose calcium, strontium and barium salts all have been prepared and studied.[2] In the case of 34 of these acids it was found that their calcium, strontium and barium salts are all three analogous in composition; *i. e.*, if the salt of one of these metals is anhydrous, so also are the salts of the other two. If one, say the calcium salt of any given acid contains 6 molecules of water of crystallization, then the corresponding strontium and barium salts are found to contain the same number. Secondly, in the case of 79 of these acids, the salts of two of these metals were observed to be analogous in composition; *i. e.*, either the calcium or strontium, or the calcium and barium, or the strontium and barium salts of a given acid resemble each other in the sense that, if the salt of either of these metals is anhydrous, so also is the salt of one of the others; or if one salt, say the calcium, contains a certain number of molecules of water of crystallization, then either the strontium or barium salt is found to contain the same number.

It is believed that these analogies in composition of calcium, strontium and barium salts are sufficiently numerous to warrant the following generalization:

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[1] As stated above, this comparison includes the anhydrous as well as the hydrated forms of the salts of these metals. It is believed that the former should be included in any general consideration of these elements. It is certainly just as characteristic that barium should form an anhydrous sulphate as it is that its chloride contains two molecules of water of crystallization.

[2] It would require entirely too much space to give even abbreviated symbols representing the composition of these salts. The names of these acids will be found in Table I, p. 287, together with the list of exceptions on p. 284.

Of the calcium, strontium, and barium salts of any acid, all or two of the salts of these metals will be found to be analogous in composition.

In support of this conclusion there are, in the first place, the salts of 113 acids out of the 141, where calcium, strontium and barium salts have all been described, and whose analogies have already been discussed; in addition to which we have also the salts of 139 acids[1] of which the salts of only two of these metals have been described in the literature, which two salts, however, are analogous in composition.[2]

The salts of 252 acids out of 280, exhibit analogies in composition in conformity to the above rule. Among those acids, whose calcium, strontium and barium salts have all been described, numbering 141, there are 28 whose salts do not show their analogies.

These are:

Amidoisophthalic,
Hippuric,
Adipic,

Ethylsuccinic,
Dibrombenzoic,
Bromnitrobenzoic,

---

[1] Want of space prevents even giving the names of these 139 acids. If there are any who are especially interested in this line of work, I will be glad to supply them with this list of acids and such of their calcium, strontium and barium salts as have been described.

[2] It is somewhat surprising to find how very considerable is the number of acids described in the literature, of which no salt has been prepared at all. Again there are quite a number of acids, only one of whose salts is described, usually the silver or the barium; and again quite a considerable number of others of which salts of only two of the metals under consideration are described. Of these, the calcium and barium salts are the two most often described, though of course the calcium and strontium and the strontium and barium are sometimes given. As stated above, in the case of 139 acids, the only two salts of the metals of calcium family described are analogous in composition. In the case of probably the same number of acids, certainly not more, the only two salts of these metals which are described are not analogous in composition. This, however, does not show necessarily that the calcium, strontium and barium salts of these do not conform to the above rule. For example, in the case of α-β-dichloracrylic and β_2-dichloracrylic acids, only the calcium and barium salts have been prepared. In the case of β_2-dichloracrylic acid, the calcium and barium salt each contains 2 molecules of water of crystallization, hence β_2-dichloracrylic conforms to the rule. In the case of the α-β-dichloracrylic acid, however, the calcium salt contains 3 and the barium salt 1 molecule of water of crystallization; hence it might be argued that the salts of this acid show an exception to the rule. As a matter of fact this is simply one of those cases in which the data are too incomplete to justify any positive conclusion. The strontium salt yet remains to be prepared; it may happen, and in fact there are some grounds for believing that it will happen, that this salt will contain the same amount of water of crystallization as either the calcium or barium salt; or even two hydrates of it may be found to exist, one corresponding to the calcium, the other to the barium salt, when in either case the analogies would conform to the rule.

Chlornitrobenzoic,
Retenedisulphonic,
Mesitylenesulphonic,
u-Durenesulphonic,
Saccharic,
Dibrom-(*o*)-amidobenzoic,
αα-Dibrompropionic
Trichlorbenzoic,
Deconic,
Lactic,
Carboxyamidobenzoic,
Bromnitrotoluenesulphonic,
Dimethylsuccinic,
Nitroisophthalic,
Gallic,
Isopimelic,
Terephthalic,
Permanganic,
Dichromic,
Metatungstic,
Chlorplatinous,
Platiodonitrous.

Without in any way attempting to explain these exceptions, it is to be observed first that in the case of several of these acids there exist discrepancies in the literature in regard to the composition of their salts. This is true of four of the above acids, *viz.*, gallic, nitroisophthalic, dibrombenzoic and carboxyamidobenzoic. According to Watts' Dictionary the salts of these do not show the analogies under discussion; whereas, according to Beilstein, at least two of their salts are analogous. Plainly, therefore, these acids have to be omitted from the discussion until these discrepancies can be cleared up.

Secondly, it should be borne in mind, in this connection, that the acids, whose salts are under discussion, represent the greatest diversity in composition and properties; and the determination of the composition of their salts represents the work of a very large number of men. Such being the case, it would seem probable, at least, that quite a number of errors in the composition of these salts must of necessity have crept into the literature. This is rendered all the more probable in the case of hydrates, for the reason that, in these compounds the water of crystallization is often determined by difference.

Lastly, it should be remembered that in many instances, even in the case of many of the salts of the acids here under discussion, not only one or two, but even several perfectly distinct hydrates of the same salt have been obtained. In view of which, it can hardly seem far-fetched to suppose that as the result of future investigation, other hydrates of those calcium, strontium and barium salts now forming the above exceptions, will be discovered of such a character as to exhibit the analogies in question.

There is another interesting feature of the results. This question naturally suggests itself regarding the resemblances which have been pointed out above, *viz.*, are these resemblances greater between the salts of calcium and strontium than between those of strontium and barium, or those of calcium and barium ; or are these resemblances about equally distributed between the salts of these three metals ? Or, in other words, do these metals also show themselves alike, or different in this respect, or do they exhibit something of a graduation of properties, so far as these analogies in the composition of their salts are concerned?

The arrangement of the acids, whose calcium, strontium and barium salts are described in the literature, as given in the following table, is intended to show whatever relation may exist in this regard.

Table No. I.

I. Acids whose calcium, strontium and barium salts are all analogous.	II. Acids whose calcium and strontium salts are analogous.
Aconitic,	Hydrochloric,
Diglycollic,	Salicylic,
Nitroamidobenzoic [3 : 2 : 1],	Anisic,
p-Nitrotoluene-(*o*)-sulphonic,	Nitric,
Amylmalonic,	Sulphocyanic,
Trichloracetic,	Citraconic,
Isoamylsulphonic,	Butyric,
Pyrotartaric,	Isobutyric,
Oxalic,	Glycollic,
Oxyazelaïc,	Iodic,
Ricinoleic,	*p*-Iodobenzoic,
Isosaccharic,	Cumene-(α)-sulphonic,
Sebacic,	Phenylglyoxylic,
Stearic,	Quinic,
Sulphuric,	Tartaric,
Uramidic,	Racemic,
Bromic,	Hydrobromic,
Triethylacetic,	Citric,
Fumaric,	Lauric,
Hydrofluoric,	Fluosilicic,
Molybdic,	Fluostannic,
Iodoauricyanhydric,	Hypophosphorous,
Nitrous,	Imidosulphonic,
Dithionic,	Tetraboric,
Plumbic,	Phosphorous,
Sulpharsenic,	Platinocyanic,
Dimesoperiodic,	Perbromplatinocyanhydric,
Orthoperiodic,	Perchloric,
Orthophosphoric,	Telluric,
Tellurous,	Tungstic,
Uranic,	Metavanadic,
Zirconic,	Chlorplatinic.
Carbonic,	
Chromic.	
Total 34	Total 32

Table No. I—Continued.

III.

Acids whose calcium and barium salts are analogous.

Nitro- (*o*)-oxybenzoic,
p-Nitrocinnamic,
Citric,
Isoheptylic,
Ferrocyanic,
Formic,
Acetic,
(*p*-*N*)-Cuminic,
Chloracetic,
Chloric,
Ethylsulphuric,
Isoheptoïc,
(γ)-Chlorisophthalic,
Propionic,
Maleïc,
Malonic,
Tolylene (*m*) diaminesulphonic
Propionic,
Citraconic,
Arsenious,
Malic,
Chlorstannic,
α-Bromacrylic,
Metaboric,
Hydrocyanic.

Total 25

IV.

Acids whose strontium and barium salts are analogous.

Azelaïc,
Nitric,
Citric,
(*m*)-Nitrobenzoic,
Alloxanic,
(*m*)-Bromtoluenesulphonic,
(*p*)-Bromtoluenesulphonic,
Caffeïc,
Carbamic,
Glyceric,
N-Caproic,
Iodic,
(β)-Chlorethanesulphonic,
(*p*)-Diethylbenzenesulphonic,
Polyporic,
Prypionic,
Selenic,
Suberic,
Succinic,
Sulphurous,
Sulphopropionic,
Thiosulphuric,
Methanesulphonic,
α-Oxy-(α)-methylglutaric,
Isovaleric,
Propionic,
Arsenic,
Arsenious,
Orthophosphoric (in acid salts),
Zincic.

Total 30

From this table it can be seen at a glance that of the 113 acids included therein, there are 34 whose calcium, strontium, and barium salts are all analogous in composition. In the case of trichloracetic acid, for example, the calcium, strontium, and barium salt each crystallizes with 6 molecules of water of crystallization. Secondly, there are 32 acids whose calcium and strontium salts are analogous in composition, 25 in which the analogy has been found to exist between the calcium and barium salts, and 30 in which it exists between the salts of strontium and barium. It will be observed that, in several instances, the same acid, for example, nitric acid, appears in two columns of the above table. This is for the reason that double or even triple analogies are sometimes displayed among the calcium, strontium, and barium salts of the same acid. In the case of nitric acid, the calcium salt crystallizes with 4 molecules of water; the strontium salt may be obtained either as an anhydrous salt or with 4 molecules of water; the barium salt is anhydrous.

Hence a double analogy exists here, one between the strontium and barium salts, both of which are anhydrous; and one between the calcium and strontium salts, both of which contain 4 molecules of water of crystallization.

The results of the comparison, as set forth in the above table, would certainly seem to show that the analogy in question is about equally distributed between calcium, strontium and barium; or, in other words, that the analogy in composition of the calcium, strontium and barium salts of any given acid is just as likely to show itself between the salts of all three of these metals, or between the calcium and strontium salts of that acid, as it is between the calcium and barium salts, or those of strontium and barium, and *vice versa;* or that, so far as composition of their salts is concerned, these three metals are altogether similar.

All this of course is opposed to the conclusions of Lenssen, to which reference was made at the beginning of this paper, and according to which strontium and barium are so closely similar in general properties and show such close analogies in the composition of their salts with various acids, as to compose a closely related group or dyad within the calcium, strontium and barium group or triad itself.

In conclusion it may be said that it can hardly be the result of chance or coincidence that out of 280 acids of the most widely different composition and properties, we have 252 in which are exhibited these striking analogies and relationships in the composition of their calcium, strontium, and barium salts. As has been indicated elsewhere in this paper, our knowledge of even the salts of so small a group of metals as the alkaline earths, is still far from complete; and hence it would seem inevitable that new relations as to the composition of salts of nearly related metals will sometime be discovered; and therefore it may well be that, in such cases as that furnished by the calcium, strontium, and barium salts of mesitylenesulphonic acid; $CaA_2.5H_2O$; SrA_27H_2O; BaA_29H_2O, which now form an exception to our rule of analogies, we are in reality catching glimpses of another relationship between the salts of these metals as important and characteristic as that under consideration. It is believed, however, that the considerations advanced in the above are in keeping with the facts as they are known to us at present.

In conclusion I desire to thank Mr. Jos. Frazer, Mr. W. A. Beatty, and Miss Logan H. Warner for their very kind assistance in the arrangement and compilation of the data herein discussed.

State College of Kentucky,
Lexington, December, 1896.

Contributions from the Chemical Laboratory of the University of Illinois.

ACTION OF MERCAPTIDES ON QUINONES.

By H. S. Grindley and J. L. Sammis.

(*Preliminary Notice.*)

A few years ago Professor C. Loring Jackson and one of us[1] found that quinones, when treated with alcoholates, give compounds which belong to the class of acetals. It was proved that these substances are formed by the addition of 2 molecules of alcohol to the two carbonyl groups of the quinone. They were named by us *hemiacetals*. In this connection it was thought that the study of the action of mercaptides on quinones would be of value and of interest. The following paper contains a description of the results thus far obtained in this direction:

The action of sodium mercaptide on dichlordiphenoxyquinone was first studied, and we found that if the substances were mixed in dry ether in the proportion of 6 molecules of the former to one of the latter, a yellow crystalline salt was formed which was insoluble in the ether, but soluble in water. It was unstable, being decomposed immediately when exposed to the air. It also decomposes readily in the presence of water, forming the product tetrathioethylquinone, $C_6(S.C_2H_5)_4O_2$, which melts at 90°–91°, and gives a hydroquinone melting at 58° when treated with reducing agents.

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[1] This Journal, **17**, 577.

The tetrathioethylquinone, when treated with two equivalents of sodium mercaptide, gives the yellow crystalline salt which was formed above by treating dichlordiphenoxyquinone with 6 equivalents of the mercaptide. This substance is so unstable that so far we have not been able to prepare it pure enough for analysis, but the method of formation and the properties of this salt indicate that it is similar in structure and belongs to the same class of compounds as those obtained by Jackson and Grindley, by treating substituted quinones with alcoholates. The sodium salt, when treated with benzoyl chloride in alcohol solution, gives the compound tetrathioethylquinone-dibenzoyldithiobenzoylacetal,

$$C_6(S.C_2H_5)_4(O.CO.C_6H_5)_2(S.CO.C_6H_5)_2.$$

This substance, when treated with zinc dust and glacial acetic acid, remains unchanged. It is not affected by hydroxylamine hydrochloride.

Action of Sodium Mercaptide on Dichlordiphenoxyquinone.—In order to study this action 5 grams of dichlordiphenoxyquinone suspended in ether, were treated with sodium ethyl mercaptide, which was made by dissolving 1.95 grams of metallic sodium in 10 grams of ethyl mercaptan dissolved in about 20 cc. of pure dry ether. This gave the proportion of 6 molecules of sodium mercaptide to 1 of dichlordiphenoxyquinone. When the two substances were brought together the reaction began at once, and heat was produced, the red dichlordiphenoxyquinone being changed into a yellow crystalline substance. In order to complete the reaction, the mixture was heated on the water-bath for a few minutes. The ether solution was rapidly filtered, and the precipitate washed with ether. The yellow substance, while still moist with ether, was put into water. It dissolved at first, giving a clear solution, but on standing a short time the aqueous solution underwent a decomposition, a green crystalline body separating.

This decomposition in water takes place slowly and seems to be assisted by exposing the aqueous solution to the action of the air. The decomposition-product was filtered off and, after washing with water, was purified by recrystallization from hot alcohol until it showed the constant melting-point of 91°. The analysis of the substance dried over sulphuric acid for several days gave the following results:

I. 0.2061 gram substance gave on combustion 0.3680 gram CO_2 and 0.1145 gram H_2O.

II. 0.2203 gram substance gave on combustion 0.3932 gram CO_2 and 0.1200 gram H_2O.

III. 0.1199 gram substance gave, on fusion with sodium carbonate and potassium nitrate, 0.3207 gram $BaSO_4$.

IV. 0.1892 gram substance gave on fusion with sodium carbonate and potassium nitrate, 0.5069 gram $BaSO_4$.

	Calculated for $C_6(S.C_2H_5)_4O_2$.	Found.			
		I.	II.	III.	IV.
C	48.27	48.67	48.67	....	....
H	5.75	6.17	6.05	....	....
S	36.78	....	....	36.72	36.80

From these results it is evident that the substance is tetrathioethylquinone. This same product is also formed by treating chloranil with sodium mercaptide. The yield is very small in both cases.

Properties of Tetrathioethylquinone, $C_6(S.C_2H_5)_4O_2$.—The substance crystallizes from alcohol in beautiful glossy, dark-green needles. It melts at 90°–91°. It is readily soluble in chloroform, benzol, glacial acetic acid, and carbon disulphide; soluble in ethyl alcohol, methyl alcohol, ligroïn, and ether. It is insoluble in water, either cold or hot. Tetrathioethylquinone is soluble in strong sulphuric acid, but is precipitated from the solution unchanged on the addition of water. It is insoluble in cold or warm concentrated hydrochloric acid. It is soluble in concentrated nitric acid with the evolution of oxides of nitrogen. It imparts a beautiful red coloration to the acid and is not reprecipitated on the addition of water. The nature of this reaction will be studied in this laboratory at an early date. It is easily reduced to the corresponding hydroquinone by the action of glacial acetic acid and zinc dust.

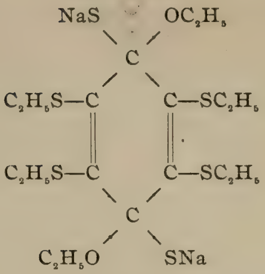
Tetrathioethylhydroquinone, $C_6(S.C_2H_5)_4O_2H_2$.—This substance was made by reducing the tetrathioethylquinone with glacial acetic acid and zinc dust. Three grams of the tetrathioethylquinone were warmed on the water-bath with these reagents until the dark-green color of the original had completely disappeared. Water was then added, and the precipitated hydroquinone was purified by recrystallizing it from alcohol containing a little hydrochloric acid to prevent oxidation. On analysis the following result was obtained :

0.24935 gram substance gave on fusion with sodium carbonate and potassium nitrate 0.6619 gram $BaSO_4$.

	Calculated for $C_6(SC_2H_5)_4(OH)_2$.	Found.
S	36.57	36.46

Properties of Tetrathioethylhydroquinone.—It crystallizes from alcohol in large colorless prisms, which melt at 58°–59°. It is insoluble in water; soluble in ligroïn, methyl alcohol, or ethyl alcohol; readily soluble in glacial acetic acid, benzol, or ether; very readily soluble in chloroform. The tetrathioethylhydroquinone dissolves in concentrated sulphuric acid, giving the acid a light-green color. It dissolves in concentrated nitric acid with effervescence, giving the solution a bright-red color. The addition of water does not cause the separation of anything. Concentrated hydrochloric acid has no effect upon the hydroquinone.

Tetrathioethylquinonedibenzoyldithiobenzoylacetal, $C_6(S.C_2H_5)_4(O.CO.C_6H_5)_2(S.CO.C_6H_5)_2$.—This substance was prepared from the yellow crystalline salt of sodium obtained as described above by the action of sodium mercaptide on tetrathioethylquinone. The method of formation and the properties of this salt are so similar to the salts of the hemiacetals of quinone obtained by Jackson and Grindley that for the time we have assumed it to have an analogous constitution which would be represented by the following structural formula :



It is then the sodium salt of tetrathioethylquinone-dithioethylhemiacetal. This salt is so very unstable that so far we have not succeeded in getting it pure enough for analysis. However, we hope by further study to obtain this salt sufficiently pure to make determinations of the amount of sodium present.

The tetrathioethylquinonedibenzoyldithiobenzoylacetal was obtained by treating the above sodium salt (which was prepared in ether and kept covered with a layer of the same to prevent decomposition) with benzoyl chloride. Action took place readily, the yellow salt going into solution and sodium chloride separating. After the action was complete the ether was removed by evaporation and the residue was treated with a dilute solution of sodium carbonate to remove the benzoic acid formed. After this treatment there was left a semiliquid residue, which on treatment with alcohol immediately became a crystalline solid. This solid was recrystallized from alcohol until it showed a constant melting-point of 131°–132°. The analysis of the substance, dried at 100°, gave the following results:

I. 0.2123 gram substance gave on combustion 0.4718 gram CO_2 and 0.11085 gram H_2O.

II. 0.2267 gram substance gave on combustion 0.5050 gram CO_2 and 0.1075 gram H_2O.

III. 0.2238 gram substance gave on fusion with Na_2CO_3 and KNO_3, 0.37255 gram $BaSO_4$.

IV. 0.11514 gram substance gave, on fusion with Na_2CO_3 and KNO_3, 0.19215 gram $BaSO_4$.

	Calculated for $C_6(S.C_2H_5)_4(O.CO.C_6H_5)_2(S{\cdot}CO.C_6H_5)_2$.	Found. I.	II.	III.	IV.
C	60.57	60.60	60.74	....	....
H	4.81	5.80	5.26	....	....
S	23.07	....	....	22.88	22.92

The analysis of this substance was very difficult, owing to the high percentage of sulphur, and the high percentages of hydrogen found were undoubtedly due to this cause.

Properties of Tetrathioethylquinonedibenzoyldithiobenzoylacetal.—It crystallizes from alcohol in two distinct forms, which are easily changed from the one to the other. When the solution is concentrated and cooled quickly the crystals form as long slender prisms. When the alcoholic solution is not so concentrated and is cooled slowly the crystals form as rhombic plates. It melts at 131°–132° and is readily soluble in benzol, chloroform, or ether; soluble in ethyl alcohol, methyl alcohol, or glacial acetic acid. It is insoluble in water or ligroïn.

The study of the action of mercaptides on quinones will be continued in this laboratory.

URBANA, ILL., Jan. 24, 1897.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

THE ACTION OF SODIUM ETHYLATE ON AMIDE BROMIDES.

BY S. E. SWARTZ.

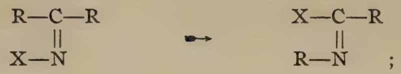
In 1881–2 A. W. Hofmann[1] developed a method for the formation of amines from acid amide bromides by treatment with caustic alkali, and proved that, in the course of the reaction, an isocyanate is first formed, which, by treatment with silver carbonate, he was able to isolate:

$$2C_2H_3ONHBr + Ag_2CO_3 = CH_3NCO + 2AgBr + H_2O + CO_2.$$

Hoogewerf and Van Dorp[2] improved the conditions of the reaction by using potassium hypobromite, and pointed out that the peculiar rearrangement which takes place in the molecule is perfectly analogous to the so-called Beckmann's rearrangement of ketoximes:

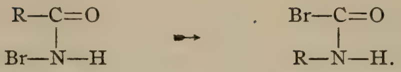
[1] Ber. d. chem. Ges., **14**, 2725; **15**, 407, 725, 762.

[2] Rec. Trav. Chim., **9**, 33; **10**, 4.



$$\begin{array}{l}\mathrm{R{-}C{-}R}\\ \quad\ \|\\ \mathrm{X{-}N}\end{array} \longrightarrow \begin{array}{l}\mathrm{X{-}C{-}R}\\ \quad\ \|\\ \mathrm{R{-}N}\end{array}\ ;$$

so also



$$\begin{array}{l}\mathrm{R{-}C{=}O}\\ \quad\ |\\ \mathrm{Br{-}N{-}H}\end{array} \longrightarrow \begin{array}{l}\mathrm{Br{-}C{=}O}\\ \quad\ |\\ \mathrm{R{-}N{-}H.}\end{array}$$

The resulting bromformamides lose hydrobromic acid when treated with silver carbonate; with potassic hydrate they yield potassic carbonates (RNHCOOK), which Hoogewerf and Van Dorp were able to isolate in many cases, and which by saponification or treatment with acids yield amines. In the presence of an acid amide, the isocyanate or bromformamide unites with it, forming an acyl urea. For instance, acetamide bromide with potassic hydrate and acetamide gives as a final product acetyl methylurea.[1]

$$CH_3CONHBr + KOH + CH_3CONH_2 = \begin{array}{l}CH_3HN\\ CH_3COHN\end{array}\!\!>CO + KBr + H_2O.$$

Lengfeld and Stieglitz have shown that when paranitrobenzamide bromide[2] or succinimide bromide is acted upon by sodium methylate, a similar arrangement is effected, giving urethanes by the action of methyl alcohol on isocyanates.

Work done in this laboratory by Mr. O. K. Folin[3] has shown, that, in general, when other amide bromides are treated with sodium methylate in methyl alcohol solution an analogous change takes place.

$$RCONHBr + CH_3OH = BrCONHR + NaOCH_3 = CH_3O.CO.NHR + NaBr.$$

In no instance has the bromine been directly replaced by the oxymethyl group.

Since molecular rearrangement of acid amide bromides is effected by a methyl alcohol solution of sodium methylate as well as by an aqueous solution of sodium hydroxide, and since, in these solutions, these substances not only exist as such but also are, to a greater or less extent, ionized, it was thought not impossible that by diminishing the electrolytic dissociation the rearrangement might be prevented and direct substitution effected.

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[1] Ber. d. chem. Ges., **14**, 2725.

[2] This JOURNAL, **15**, 215; 504, **16**, 307.

[3] The results will be published in the next number of this JOURNAL.—ED.

At the suggestion of Drs. Lengfeld and Stieglitz the study of this question was undertaken by me. Dry succinimide bromide was treated with dry sodium methylate with and without a diluent, and, since ethyl alcohol causes a far smaller degree of electrolytic dissociation than methyl alcohol, various amide bromides which were found to suffer rearrangement in methyl alcohol were treated with a solution of sodium ethylate in ethyl alcohol.

It was found that succinimide bromide, treated with dry sodium methylate, regenerated succinimide, that no rearrangement took place, and that, at the same time bromine was not replaced by the methoxy group (CH_3O), but that the imido bromide was saponified or reduced, regenerating succinimide : with sodium ethylate in ethyl alcohol, in every case rearrangement was effected, and in no instance was any derivative of hydroxylamine obtained. The results obtained were perfectly analogous to those of Lengfeld and Stieglitz, and O. K. Folin, by the action of sodium methylate in methyl alcohol.

EXPERIMENTAL PART.

I. *The Action of Dry Sodium Methylate on Succinimide Bromide.*

Succinimide bromide, prepared according to the method described by Lengfeld and Stieglitz,[1] was dried for six days on clay plates over sulphuric acid in a vacuum desiccator, and the substance then carefully pulverized in a dry mortar. Sodium methylate was prepared immediately before using from absolute methyl alcohol, and was freed from alcohol in the usual way. The benzene was dried over sodium for four days and distilled.

Five grams of succinimide bromide and 1.6 grams of sodium methylate with 25 cc. benzene were heated in a sealed tube at 100° for two hours. On opening the tube a considerable quantity of gas escaped. The tube contained a dark red liquid, in which the odor of pyrrol was strong, and some undissolved material. The solution was neutral. Testing a portion with a hydrochloric acid solution of potassium iodide, there was no coloration, which indicated that no unchanged imide bromide remained. The contents of the tube were then extracted with hot benzene from which, on cooling, crystals were obtained which from their crystal form, solubility, and melting-point (125°) were identified as succinimide. The mother-liquor was then evaporated to dryness, and taken up with ether, and the colored solution digested with bone-black when the color disappeared. Ligroïn now precipitated more succinimide, and on distilling the ligroïn-ether solution a slight residue of almost pure succinimide remained. Washing the residue, insoluble in hot benzene, with water, there was obtained on evaporation the theoretical quantity of sodium bromide. While there remained insoluble in water and hot alcohol a tarry mass which amounted to almost 50 per cent. of the organic matter engaged in the reaction.

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[1] This JOURNAL, **15**, 217.

When 10 grams of succinimide bromide and 3.2 grams of sodium methylate in 100 cc. of benzene were heated under a reversed condenser the reaction was complete in four hours, no succinimide bromide remaining. The solution, which was a dark red, had a strong odor of pyrrol. Treated as above, it was found to contain about 70 per cent. of the theoretical amount of succinimide, and considerable tar, but no urethane or substituted hydroxylamine.

An attempt was made to study the effect of sodium methylate without a diluent on succinimide bromide, but the result was far from satisfactory, for when molecular quantities of the methylate and imide bromide were shaken together the action was explosively violent. When the imide bromide was added in small quantities, chemical change took place with somewhat less violence but was still very energetic. There resulted a black semi-charred mass with the odor of pyrrol, which, treated as above, yielded succinimide amounting to about 20 per cent. of the theoretical quantity, but no other organic substances could be isolated.

II. *The Action of Sodium Ethylate on Benzamide Bromide.*

To a solution of sodium ethylate prepared from 1.5 grams of sodium in 60 grams of absolute ethyl alcohol, cooled in ice water, 12.8 grams of well dried benzamide bromide were added. Reaction began slowly, as was indicated by a gradual rise in temperature. Heated on a water-bath connected with a reversed condenser, well dried and closed with a calcium chloride tube, the solution became brownish red, and after twenty minutes, a test with acidulated potassic iodide showed that the action was complete. On cooling, a heavy precipitate appeared. The slightly alkaline solution was acidulated with a few drops of dilute acid, and then filtered. Washing the precipitate with cold water to remove the sodium bromide, and recrystallizing from hot alcohol, a substance was obtained in long white needles, melting at 199°. Subjected to dry distillation, the substance gave phenyl isocyanate, which was recognized by its odor, and benzamide (melting-point 128°). These decomposition-products, the melting-point 199°, the crystal form and solubility, together with the analysis, identify it as phenyl benzoyl urea described by Kühn.[1]

On analysis 0.2078 gram gave 21.6 cc. nitrogen at 18° and 742 mm. pressure.

	Calculated for $C_{14}H_{12}N_2O_2$.	Found.
Nitrogen	11.66	11.77

The alcoholic solution was evaporated to dryness on the water-bath and the solid residue extracted with chloroform, and dried over calcium chloride. The oil which remained was distilled under a pressure of 14–24 mm. It separated into two fractions which came over between 90°–120° and 140°–160°. The first fraction was a liquid which had a strong odor of phenyl isocyanate, and crystallized with difficulty, after standing four days. This was dried on clay plates and recrystallized from ligroïn, when a constant melting-point of 52° was obtained. This, together with its boiling-point, 238°, (750 mm.), identified the product as phenylurethane.

The higher fraction was a solid with a strong odor of benzonitrile. Recrystallizing from hot benzene, crystals were obtained which proved to be benzamide (melting-point 128°).

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[1] Ber. d. chem. Ges., **17**, 2881.

Evidently some phenyl benzoylurea remained with the oil, and on distillation it decomposed, yielding phenyl isocyanate, obtained with the urethane, and benzamide, which in turn, gave a little benzonitrile.

The yield was: Phenyl benzoylurea, 53 per cent.; phenylurethane, 15 per cent.; benzamide, 18 per cent. of the theoretical.

Repetition of the experiment varying the conditions of temperature and concentration of the alcoholic solution resulted in only a slight variation in the relative amounts of the products.

Sodium ethylate in alcoholic solution evidently acts in two ways on benzamide bromide. On the one hand, it causes a rearrangement of a part of the benzamide bromide to bromformanilide in the manner indicated above:

$$1.\ C_6H_5CONHBr \rightarrow BrCONHC_6H_5.$$

On the other hand, it reduces the benzamide bromide to benzamide, since the odor of acetaldehyde was very prominent during the reaction:

$$2.\ C_6H_5CONHBr + NaOC_2H_5 = C_6H_5CONH_2 + NaBr + CH_3CHO.$$

The bromformamide then unites to a large extent with the benzamide, forming phenyl benzoyl urea:[1]

$$3.\ C_6H_5NHCOBr + C_6H_5CONH_2 = C_6H_5NHCONHCOC_6H_5 + HBr.$$

and to some extent with sodium ethylate still present, giving phenyl urethane:

$$4.\ C_6H_5NHCOBr + NaOC_2H_5 = C_6H_5NHCO_2C_2H_5.$$

From the yield it was found that 45–55 per cent. of the benzamide bromide had suffered rearrangement, giving phenyl benzoyl urea and phenyl urethane.

III. *The Action of Sodium Ethylate on Paranitrobenzamide Bromide.*

Paranitrobenzamide bromide, prepared after the method of Hoogewerf and Van Dorp, is very difficult to wash and dry, and as potassium hydrate or water even in minute quantities furthers ionization, great care was taken to wash out all the caustic potash. The substance was then put on clay plates and dried in the open air for 24 hours, then pulverized and dried for six days in a vacuum-desiccator over sulphuric acid.

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[1] Ber. d. chem. Ges., 14, 2725.

To a well cooled solution of one gram of sodium in 100 grams of absolute alcohol, 10.5 grams of *p*-nitrobenzamide bromide were added. Reaction began slowly at the temperature of the room, and heat was necessary to complete the change. After heating on a water-bath for twenty minutes, the contents of the flask needed only a drop of dilute acetic acid to render it slightly acid. Distilling off the alcohol and extracting the residue with absolute ether, a slightly yellow solution was obtained, which on cooling in a freezing-mixture, readily yielded a precipitate of yellow needles, which, after recrystallization from ligroïn, melted at 128°. This corresponded with paranitrophenyl urethane, prepared by Häger.[1] To identify the product more definitely, the urethane was prepared synthetically from chlorcarbonic ether and paranitraniline. It proved to be identical in color, crystal form, solubility and melting-point, with the body above described.

The action of sodium ethylate in alcoholic solution on paranitrobenzamide bromide, causes a rearrangement, yielding a urethane similar to that produced when it reacts with benzamide bromide:

1. $NO_2C_6H_4CONHBr + NaOC_2H_5 = NO_2C_6H_4NHCOBr + NaOC_2H_5.$

2. $NO_2C_6H_4NHCOBr + NaOC_2H_5 = NO_2C_6H_4NHCO_2C_2H_5 + NaBr.$

The residue left after extracting with ether was washed to remove the sodium bromide, and the remaining solid dissolved in hot alcohol. On cooling, a reddish brown precipitate was obtained, which after several precipitations, melted at 256°. The crystals are fine needles with a distinct yellow color, insoluble in cold alcohol, ether, ligroïn, chloroform, and acetone, and slightly soluble in hot alcohol.

The method of formation suggested, and the analysis proved, this to be symmetrical paranitrophenyl-paranitrobenzoyl urea.

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[1] Ber. d. chem. Ges., **17**, 2625.

On analysis 0.1203 gram gave 18.8 cc. nitrogen at 742 mm. and 23°.

	Calculated for $C_{14}H_{10}N_4O_6$.	Found.
Nitrogen	16.98	17.16

It is formed according to the following reactions:

1. $NO_2C_6H_4CONHBr + NaOC_2H_5 = NO_2C_6H_4NHCOBr + NaOC_2H_5$.

2. $NO_2C_6H_4NHCOBr + NaOC_2H_5 = NO_2C_6H_4CONH_2 + NaBr + CH_3CHO$.

3. $NO_2C_6H_4NHCOBr + NO_2C_6H_4CONH_2 = NO_2C_6H_4NHCONHCOC_6H_4NO_2 + HBr$.

On adding water to the alcoholic solution from which *p*-nitrophenyl-*p*-nitrobenzoyl urea had been separated, crystals were obtained, which were found to be paranitrobenzamide.

The yield was: urethane, 20 per cent.; amide, 60 per cent.; urea, 15 per cent.

In greater concentrations (40 grams of absolute alcohol and 1 gram of sodium) no urea was obtained, but a higher per cent. of urethane (30–40), and a lower per cent. of the amide (50–55) resulted. One gram of sodium in 75 grams absolute alcohol gave analogous results. Yield: urethane, 30 per cent.; amide, 55 per cent.; urea, 10 per cent.

These results show that sodium ethylate in alcoholic solution acts in a perfectly analogous manner upon benzamide bromide and paranitrobenzamide bromide.

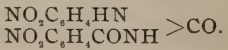
IV. *The Action of Sodium Ethylate on Orthonitrobenzamide Bromide.*

Orthonitrobenzamide bromide was prepared in the same manner as the corresponding para compound, 10.5 grams being added to a solution of one gram of sodium in 40 grams of absolute alcohol carefully cooled. The liquid turned slightly red, and part of the bromide went into solution, but it was necessary to heat on the water-bath to complete the reaction, but for a shorter time than in the case of paranitrobenzamide bromide. At the end of seven minutes the amide bromide had completely disappeared. Acidifying with two drops of dilute acetic acid and cooling, a yellow precipitate was obtained. The alcoholic solution was evaporated to dryness and the residue, together with the precipitate was washed with cold water to remove the sodium bromide. After drying on clay plates, and extracting with ether, ligroïn precipitated from the solution an almost white crystalline body, which melted at 212°. Concentrating the ether-ligroïn solution, and cooling in a freezing-mixture, sulphur yellow crystals were obtained, which dissolved quite readily in warm ligroïn (boiling-point 40°–60°), and were again precipitated on cooling. These melted at 58°, and appeared to be identical with orthonitrophenyl urethane obtained by Rudolph.[1]

To identify it more fully the carbamic ester was synthetically prepared from orthonitraniline and chlorcarbonic ether. The two substances were identical.

The crystals melting at 212°, together with the residue left after extracting with ether, were digested with boiling ether. After filtering, the cooled filtrate gave an almost white precipitate which, crystallized from acetone, melted at 220°. This substance is difficultly soluble in ether, acetone, benzene and chloroform, but it dissolves readily in hot alcohol from which it is precipitated with difficulty on cooling, but the addition of water causes it to separate out very readily.

The method of formation and analysis show this to be orthonitrophenylorthonitrobenzoyl urea,



$$\begin{matrix} NO_2C_6H_4HN \\ NO_2C_6H_4CONH \end{matrix} > CO.$$

On analysis 0.2037 gram gave 32 cc. nitrogen at 25° and 741 mm.

	Calculated for $C_{16}H_{10}N_4O_6$.	Found.
Nitrogen	16.98	17.13

To identify this body more fully, it was synthetically prepared by adding to an ethereal solution of orthonitrophenyl isocyanate the theoretical quantity of orthonitrobenzamide, which immediately yielded a precipitate identical with the above described urea :

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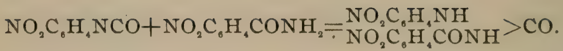
[1] Ber. d. chem. Ges., **12**, 1295.



$$\mathrm{NO_2C_6H_4NCO + NO_2C_6H_4CONH_2 = \begin{matrix} NO_2C_6H_4NH \\ NO_2C_6H_4CONH \end{matrix} > CO.}$$

From the residue left after digesting with boiling ether, a small amount of orthonitrobenzamide was obtained by extracting with hot alcohol and precipitating by adding water. The yield from the reaction was as follows: urethane, 20 per cent.; urea, 60 per cent.; amide, 10 per cent.

A change in concentration of the alcoholic solution modified the relative amounts of the products to a slight extent, but gave no new substances.

One gram of sodium in 50 grams of absolute alcohol, with a molecular quantity of the amide bromide yielded of urethane, 30 per cent.; of urea, 50 per cent.; of amide, 10 per cent.

Change in conditions of temperature did not effect the results to any great degree.

IV. *The Action of Sodium Ethylate on Metanitrobenzamide Bromide.*

Metanitrobenzamide bromide was prepared in the same manner as paranitrobenzamide bromide. 10.5 grams of it were added to 1 gram of sodium in 100 grams of absolute alcohol. Chemical change took place more slowly than in the case of orthonitrobenzamide bromide, since no heat was manifested, and a longer time, 20 minutes, of heating on the water-bath was required to decompose the amide bromide.

During the reaction the odor of acetaldehyde was very strong. The slightly alkaline solution was acidified by a few drops of acetic acid, and freed from alcohol by heating on the water-bath. The residue was extracted with chloroform. From the chloroform solution, ligroïn precipitated metanitrobenzamide (melting-point 141°).

Distilling off the chloroform and ligroïn and taking up the residue with ether, ligroïn precipitated yellow needles which dissolved readily in low-boiling ligroïn (30°–40°), and were precipitated again on cooling in a freezing-mixture. These melted at 65°.

The method of formation indicated that this was metanitrophenyl urethane. To identify it more fully the carbamate was synthetically prepared from metanitraniline and chlorcarbonic ether, and the product thus obtained proved to be identical with that crystallized from ligroïn. Analysis gave the following results:

0.1772 gram gave 21.6 cc. nitrogen at 20° and 743 mm.

	Calculated for $C_9H_{10}N_2O_4$.	Found.
Nitrogen	13.33	13.5

Metanitrophenyl urethane is a yellow substance which crystallizes in fine needles from ligroïn. It is readily soluble in ether, alcohol, chloroform, benzene and acetone. In ligroïn it dissolves more readily than the corresponding ortho or para compounds. It is almost insoluble in water. In alkalies it dissolves with difficulty with slight coloration. Heated in dilute alkalies it saponifies, yielding metanitraniline.

The yield was: urethane, 10 per cent.; amide, 80–90 per cent.

A change in the concentration of the alcoholic solution effected a change in both the relative quantities and the kind of products.

1. In quite dilute solutions, 1 gram of sodium in 300 grams of absolute alcohol and 10.5 grams of metanitrobenzamide bromide, the reaction was complete in 15 minutes when heated on the water-bath. The solution was strongly alkaline, and, on adding dilute acetic acid to neutralize, considerable carbon dioxide was given off. On allowing the solution to stand, an almost white crystalline body appeared, which melted at 230° and was identical with metanitrophenylmetanitrobenzoyl urea prepared by O. K. Folin[1] from metanitrophenyl isocyanate and benzamide.

When the alcohol was driven off from the filtrate from which the urea had been obtained, the residue was extracted with ether. From this solution ligroïn precipitated a mixture of metanitrobenzamide and metanitraniline. These were separated by dissolving out the nitraniline with ether in which the amide is very difficultly soluble. The amide was identified by its melting-point, 141°.2, its solubility and general appearance. The metanitraniline melted at 109°. In chloroform solution with dry hydrochloric acid it formed the hydrochloride.

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[1] See note, p. 296.

Concentrating the ether-ligroïn solution from which nitraniline and nitrobenzamide had been obtained and cooling to —17° yellow crystals were obtained which melted at 65°, and were identical with the metanitrophenyl urethane previously obtained.

The yield was: urethane, 6 per cent.; amide, 15 per cent.; nitraniline, 55 per cent.; urea, 15 per cent.

2. In very dilute solutions, 1 gram of sodium in 600 grams absolute alcohol, and 10.5 grams of metanitrobenzamide bromide, treated in the same manner as above, no urea was obtained, but other products in the following proportion: Urethane, 6 per cent.; amide, 30 per cent.; nitraniline, 60 per cent.

3. In somewhat concentrated solution, 1 gram of sodium in 60 grams of alcohol there resulted 6 per cent. of urethane and 80–90 per cent. of the amide, and a small quantity of tar. No urea or nitraniline could be found.

4. In more concentrated solutions, 1 gram of sodium in 18 grams of alcohol, the yield was: urethane, traces; amide, 80–90 per cent.; tar, 5–10 per cent.

5. To study the effect of the presence of water when the amide bromide is treated with sodium ethylate, one gram of sodium was added to 60 grams of 98.5 per cent. alcohol, and to the cooled solution were added 10.5 grams of metanitrobenzamide bromide. No more heat was manifested than when the same concentration of absolute alcohol solution was used. The liquid became wine red on heating twenty minutes on the water-bath, when a portion tested with acidified potassium iodide, showed the presence of unchanged amide bromide. The substance then stood in the flask at the temperature of the room over night, when the action was found to be complete. In the flask was found a precipitate of metanitrophenylmetanitrobenzoyl urea. In the filtrate the urethane and amide were found but no nitraniline. The yield was as follows: Urethane, 5–7 per cent.; amide, 25–35 per cent.; urea, 40–50 per cent.

6. In 60 grams of 75 per cent. alcohol the same amounts of

amide bromide and sodium ethylate gave only the amide, 80–90 per cent., and tar.

It is evident that the course of the reaction is in principle analogous to that described as taking place when sodium ethylate reacts with benzamide bromide, although the number of products is different. The nitrophenyl urethane, $NO_2C_6H_4$-$NHCOOC_2H_5$, the nitrophenylnitrobenzoyl urea, $NO_2C_6H_4$-$NHCONHCOC_6H_4NO_2$, and the nitraniline, $NO_2C_6H_4NH_2$, are all products of the rearrangement of nitrobenzamide bromide $NO_2C_6H_4CONHBr$. From experiments 1 and 2 it is seen that in very dilute solution a very large amount (60–80 per cent.) of the amide bromide suffered rearrangement, so that in this fundamental manner sodium ethylate in ethyl alcohol acts just as sodium methylate in methyl alcohol,[1] or an aqueous solution of alkalies. The formation of free nitraniline in very dilute solutions is interesting, as it must be due to the saponification of the isocyanate, $NO_2C_6H_4NCO$, by the alkali, while in concentrated solution where there is less electrolytic dissociation such saponification does not seem to take place to any extent. Lengfeld and Stieglitz[2] observed the formation of paranitraniline in an analogous reaction where paranitrobenzamide bromide reacted with dilute sodium methylate in methyl alcohol. In this case in accordance with the stronger electrolytic dissociation of methyl alcohol solutions, the saponification occurs very prominently in a dilution of 1 : 100. The addition of a little water (Ex. 5) to a solution of sodium ethylate, 1 : 60, has the same effect. On increasing the electrolytic dissociation by this means the more concentrated solution gives considerable nitraniline.

V. *The Action of Sodium Ethylate on Succinimide Bromide.*

1. To 40 grams of absolute alcohol 1 gram of sodium was added, and to the cooled solution 8 grams (1 mol.) of well dried succinimide bromide. The sodium became slightly warm and the color changed to reddish brown. Heated twenty minutes on the water-bath the reaction was complete. On neutralizing the slightly alkaline solution with dilute acetic acid, and distilling off the alcohol, there remained a

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[1] Lengfeld and Stieglitz: This JOURNAL, **15**, 215.

[2] This JOURNAL, **16**, 370.

dark brown mass. This was extracted several times with chloroform. On cooling the solution, crystals were obtained which melted at 125° and were identified as succinimide. On concentrating the mother-liquor and adding ligroïn, at first more succinimide was precipitated. This was filtered off. An addition of more ligroïn now precipitated a silver-white, flaky, crystalline body, resembling very strongly in general appearance acetanilide. This recrystallized from ligroïn (boiling-point 30°–40°), melted at 78°. There was obtained less than 5 per cent., nor was the yield increased by repetition of the experiment.

2. On varying the conditions of the experiment the concentration was increased to 1.5 grams of sodium in 40 grams of absolute alcohol, and the molecular quantity of succinimide bromide, on cooling the solution. After the more energetic action had ceased the flask, closed with a calcium chloride tube, stood until succinimide bromide was no longer present in the solution. This took three days. The strongly alkaline solution was acidified with dilute acetic acid, which caused carbon dioxide to escape. Treating the contents of the flask as in experiment 1, there resulted almost 5 per cent. of the substance melting at 78°, and 60 per cent. of succinimide.

3. One gram of sodium was added to 40 grams of absolute alcohol and the solution was warmed to 45° when the molecular quantity of succinimide bromide was added in small portions. The action was very energetic, and at the end of ten minutes all the imide bromide had disappeared. The solution was slightly alkaline and when acidified with acetic acid gave off no carbon dioxide. Concentrating and extracting as before about 60 per cent. of succinimide was obtained, together with considerable tar, and less than 3 per cent. of the substance melting at 78°.

Several other conditions of temperature and of dilution of alcoholic solution did not essentially effect the yield. In general there resulted, of succinimide, 50–80 per cent.; of the substance melting at 78°, 3–5 per cent.; of tar, 10-30 per cent.

Analysis of the substance melting at 78° showed it to have the composition represented by the formula $C_6H_{10}NO_3$.

I. 0.2098 gram substance gave 18.2 cc. nitrogen at 18° and 746 mm.

II. 0.1827 gram substance gave 16.3 cc. nitrogen at 25° and 743 mm.

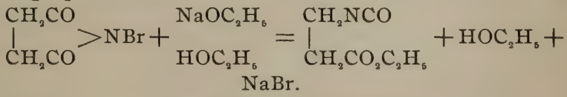
III. 0.1642 gram substance gave 0.2970 gram CO_2 and 0.1087 gram H_2O.

IV. 0.2293 gram substance gave 0.4196 grams CO_2 and 0.1571 gram H_2O.

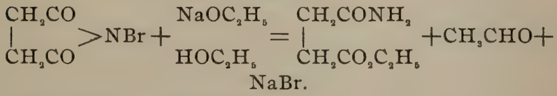
	Calculated for $C_6H_{10}N_2N_6$.	Found. I.	II.	III.	IV.
Nitrogen	9.72	9.83	9.75	....	....
Carbon	50.00	....	....	49.88	49.88
Hydrogen	6.94	....	....	7.45	7.35

The method of formation and analysis indicate that this is identical in structure with the dimethyl succinylo-β-ureidopropionate obtained by Lengfeld and Stieglitz,[1] who determined its constitution and molecular weight.

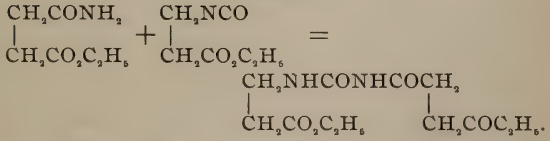
The course of the reaction may be represented by the following equations:

1. 

$$\begin{array}{l}CH_2CO\\ |\\ CH_2CO\end{array}\!>NBr + \begin{array}{l}NaOC_2H_5\\ HOC_2H_5\end{array} = \begin{array}{l}CH_2NCO\\ |\\ CH_2CO_2C_2H_5\end{array} + HOC_2H_5 + NaBr.$$

2. 

$$\begin{array}{l}CH_2CO\\ |\\ CH_2CO\end{array}\!>NBr + \begin{array}{l}NaOC_2H_5\\ HOC_2H_5\end{array} = \begin{array}{l}CH_2CONH_2\\ |\\ CH_2CO_2C_2H_5\end{array} + CH_3CHO + NaBr.$$

3. 

$$\begin{array}{l}CH_2CONH_2\\ |\\ CH_2CO_2C_2H_5\end{array} + \begin{array}{l}CH_2NCO\\ |\\ CH_2CO_2C_2H_5\end{array} = \begin{array}{lll}CH_2NHCONHCOCH_2 & & \\ | & & |\\ CH_2CO_2C_2H_5 & & CH_2COC_2H_5.\end{array}$$

Diethyl succinylo-β-ureidopropionate is a silver-white substance resembling in appearance acetanilide. It is readily soluble in ether, acetone, alcohol, benzene, and chloroform. It is quite soluble in low-boiling ligroïn, from which it may be crystallized by cooling and prolonged stirring.

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[1] This JOURNAL, **15**, 219.

The formation of the ethyl ester of carboethoxy-β-ureidopropionic acid, corresponding to the methyl ester obtained by Lengfeld and Stieglitz,[1] could not be accomplished.

The action of sodium ethylate in a solution of ethyl alcohol upon amide and amide bromides is twofold. It acts first as a reducing-agent regenerating the acid amide; secondly, as a rearranging-agent changing the amido bromide to a bromformamide or isocyanate. The isocyanate may then react, first, with the alcohol present forming a urethane; second, with the acid amide generated by reduction of the amide bromide forming a symmetrical substituted urea; or, third, it may be saponified, forming the amine. The reaction is perfectly analogous to that of methyl alcoholate in a solution of methyl alcohol or of sodium hydroxide in aqueous solution on acid amide bromides. The products of the chemical change depend upon the concentration of the solution and the kind of amide bromides employed. In very concentrated solutions sodium ethylate acts almost wholly as a reducing-agent regenerating the acid amides. In more dilute solutions rearrangement is effected and urethanes or ureas result. In very dilute solutions where the ionization is greater, the isocyanate is saponified and amines are formed.

As a method of forming urethanes the yield is much smaller than when sodium methylate is employed in a solution of methyl alcohol.

Lengfeld and Stieglitz have ascertained that chlorformanilide and phenyl isocyanate are especially easily obtained from phenyl urethane by the action of phosphorus pentachloride and, since little study has been given to the aromatic isocyanates and few of them have been prepared, the nitrophenyl urethanes obtained in the previous experiments were used to test the general applicability of Lengfeld and Stieglitz's reaction, and to study such chlorformamides and isocyanates.

1. *Chloroform-o-Nitranilide.*—Since the methyl ester of orthonitrocarbamic acid is produced almost quantitatively by the action of sodium methylate in a solution of methyl alcohol it was used instead of the ethyl ester.

In a well dried flask phosphorus pentachloride (7.2 grams) which had been previously washed with sodium-dried ligroïn (boiling-point 30°–40°), and the molecular quantity of methylorthonitrophenylurethane, and the two substances were carefully mixed by shaking. No reaction occurred at the ordinary temperature. The flask connected with a long delivery tube, which had been drawn out to a fine point, was heated on the water-bath. At 53° the urethane melted, but no chemical change was manifest. At 59° a few bubbles of gas appeared which became more numerous as the temperature was raised. At 70° the evolution of gas was quite rapid and this temperature was maintained for two hours where no more gas was formed. The escaping gas was identified as methyl chloride burning with a green-tinged flame as it escaped from the tube. On weighing the flask it was found to have decreased in weight 2.2 grams. The theoretical loss of weight for methyl chloride, CH_3Cl, was 1.86 grams. The slight excess may be accounted for by the volatility of the phosphorus oxychloride formed.

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[1] This JOURNAL, **15**, 215.

The flask now contained a slightly yellow liquid which, extracted with sodium-dried ligroïn, gave, when cooled in a freezing-mixture, white needle-shaped crystals, which, on recrystallizing from the same solvent, melted at 47°. The yield was about 70 per cent. of the theoretical for chloroformanilide, according to the equation

$$NO_2C_6H_4NHCO_2CH_3 + PCl_5 = NO_2C_6H_4NHCOCl + POCl_3 + CH_3Cl.$$

Crystals precipitated from ligroïn (boiling-point 20°–30°) and carefully pressed between filter paper, then allowed to stand twenty minutes in a vacuum-desiccator over vaseline and calcium chloride, gave the following results on analysis:

0.1612 gram heated with lime and precipitated with silver nitrate gave 0.1104 gram AgCl.

	Calculated for $C_7H_5N_2O_3Cl$.	Found.
Chlorine	17.44	16.89

The substance is very difficult to obtain pure for analysis, as it rapidly loses hydrochloric acid. When crystallized from ligroïn and dried over vaseline and calcium chloride in a vacuum-desiccator for twelve hours analysis showed a loss of 18 per cent. of the chlorine contained.

0.2172 gram, analyzed as above, gave 0.1246 gram AgCl.

	Calculated for $C_7H_5N_2O_3Cl$.	Found.
Chlorine	17.44	14.19

The substance is readily soluble in chloroform, benzene, and ligroïn. In water it colors the solution yellow, forming nitraniline (melting-point 71°–72°) :

(1) $NO_2C_6H_4NHCOCl + H_2O = NO_2C_6H_4NHCOOH + HCl$.
(2) $NO_2C_6H_4NHCOOH = CO_2 + NO_2C_6H_4NH_2$.

With methyl alcohol it forms yellow crystals which melt at 53°, and are identical with the methylorthonitrophenylurethane used as starting material. With ethyl alcohol it forms orthonitrophenylurethane melting at 58°. On standing it loses hydrochloric acid, and on long standing it changes to a white crystalline compound, which melts at 220°, insoluble or nearly so in all organic solvents.

Orthonitrophenylurethane.—The general method of preparing this was devised by Mr. O. K. Folin,[1] as a modification of the method of Lengfeld and Stieglitz for the preparation of metanitrophenyl isocyanate.

4.45 grams of phosphorus pentachloride, washed with sodium-dried ligroïn and the molecular quantity of methylorthonitrophenylurethane were heated in a flask for three hours, when no more gas was given off. The loss of weight of the flask was 1.18 grams. The calculated loss of weight in forming the chlorformanilide is 1.13 grams.

The phosphorus oxychloride was then distilled off in a current of dry hydrochloric acid. At the end of three hours the contents of the flask showed no further loss of weight. The loss was 3 grams ; calculated loss for phosphorus oxychloride, 3.3 grams. A light-brown liquid remained which was heated in a slow current of dry air at 78°–80° and then for two hours at 90°, when hydrochloric acid ceased to be given off. There now remained in the flask 3.55 grams of material. The theoretical weight of the isocyanate to be formed was 3.27 grams. On extracting with ligroïn almost all went into solution, a small quantity of tar remaining. On cooling the solution an almost white precipitate appeared which, on recrystallization, melted at 41°. The method of formation, analysis, and synthetic products showed the substance to be orthonitrophenyl isocyanate.

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[1] See note, p. 296.

I. 0.1616 gram gave 24.3 cc. nitrogen at 15° and 741 mm.

II. 0.3393 gram gave 0.6377 gram CO_2 and 0.0801 gram H_2O.

	Calculated for $C_7H_4N_2O_3$.	Found. I.	Found. II.
Nitrogen	17.04	17.23	....
Carbon	51.27	....	51.08
Hydrogen	2.44	....	2.61

Orthonitrophenyl isocyanate, *o*-$NO_2C_6H_4NCO$, is an almost white solid melting at 41°. It crystallizes readily from low-boiling ligroïn in clusters of delicate needle-shaped crystals. It dissolves readily in chloroform, ether, and benzene. On standing in the air it turns yellow. With water it forms nitraniline. With ethyl and methyl alcohol it gives the corresponding urethanes. On standing twenty days in a vacuum 5 grams changed almost completely into a substance identical with that formed by long standing of chloroformnitranilide, which is probably the polymeric product, a cyanurate.

A number of derivatives of the isocyanate was prepared.

Isopropyl o-Nitrophenylcarbamate, *o*-$NO_2C_6H_4NHCO_2C_3H_7$.—To 1 gram of isopropyl alcohol 0.5 gram *o*-nitrophenyl isocyanate was added. The reaction began immediately with evolution of heat. The solution became yellow but no precipitate appeared. On driving off the excess of alcohol there remained a yellow oil, which crystallized after prolonged stirring in a freezing-mixture, but became an oil again at the temperature of the room. The oil dissolved in ligroïn, and, on cooling and stirring, crystallized in yellow cubes, which melted at 12°.

0.1606 gram gave 17.8 cc. nitrogen at 19° and 741 mm.

	Calculated for $C_{10}H_{12}N_2O_4$.	Found.
Nitrogen	12.5	12.47

Isobutyl o-Nitrophenylcarbamate, *o*-$NO_2C_6H_4NHCO_2C_4H_9$.—

When isobutyl alcohol was treated with *o*-nitrophenyl isocyanate in ethereal solution, it yielded yellow crystals, which melted at 13° and were soluble in alcohol and ether, but less soluble in low-boiling ligroïn than the corresponding ethyl urethane.

0.1624 gram gave 17.8 cc. nitrogen at 26° and 7.45 mm.

	Calculated for $C_{11}H_{14}N_2O_4$.	Found.
Nitrogen	11.76	11.86

Normal Amyl o-Nitrophenylcarbamate, $NO_2C_6H_4NHCO_2C_6H_{11}$. —This substance was prepared by adding orthonitrophenyl isocyanate to an excess of normal amyl alcohol, and driving off the excess of alcohol by heating on an oil-bath at 137°. The yellow oil which remained crystallized at —20° and, when precipitated from ligroïn, melted at —5°.

0.1960 gram gave 19.8 cc. nitrogen at 21° and 742 mm.

	Calculated for $C_{12}H_{16}N_2O_4$.	Found.
Nitrogen	11.1	11.26

Glycol Nitropheylmonocarbamate, *o*-$NO_2C_6H_4NHCO_2C_2H_4OH$. —To 1 gram of orthonitrophenyl isocyanate in ethereal solution glycol was added in slight excess of the ratio of 1 molecule of glycol to one of the isocyanate. Repeated shaking during two hours was required to get all the glycol into solution. When the ether was distilled off there remained a yellow oil which, by repeated crystallization from ligroïn (boiling-point 20°–30°), yielded a yellow crystalline body which analyses showed to be glycol orthonitrophenylmonocarbamate.

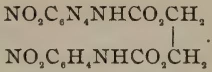
0.1932 gram gave 21.6 cc. nitrogen at 22° and 749 mm.

	Calculated for $C_9H_{10}N_2O_5$.	Found.
Nitrogen	12.39	12.54

Glycol orthonitrophenylmonocarbamate is a yellow crystalline substance which melts at 71° without decomposition. It dissolves readily in ether, alcohol, chloroform, and benzene, but with difficulty in ligroïn and water. It is not affected by alkalies or dilute acids in the cold, but when heated they readily decompose it. Its formation is expressed by the equation :

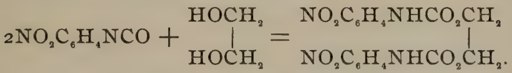
$$NO_2C_6H_4NCO + NOCH_2CH_2OH = NO_2C_6H_4NHCO_2CH_2CH_2OH.$$

Glycol o-Nitrophenyldicarbamate,



$$\begin{array}{c} NO_2C_6N_4NHCO_2CH_2 \\ | \\ NO_2C_6H_4NHCO_2CH_2 \end{array}$$

.—To an ethereal solution of 1 gram of *o*-nitrophenyl isocyanate (2 mols.), 1 molecule of glycol was added, and the solution shaken till the glycol dissolved. When the ether was distilled off the yellow oil which remained was heated on the water-bath for twenty minutes to insure complete reaction. Cooled it readily crystallized. Purified by precipitating from ether by ligroïn the melting-point remained constant at 160°. The yield is quantitative. Analysis showed the substance to be glycol orthonitrophenyldicarbamate :



$$2NO_2C_6H_4NCO + \begin{array}{c} HOCH_2 \\ | \\ HOCH_2 \end{array} = \begin{array}{c} NO_2C_6H_4NHCO_2CH_2 \\ | \\ NO_2C_6H_4NHCO_2CH_2. \end{array}$$

0.1335 gram gave 17.5 cc. nitrogen at 24° and 743 mm.

	Calculated for $C_{16}H_{14}N_6O_8$.	Found.
Nitrogen	14.36	14.44

The dicarbamate is a yellow crystalline body melting at 160°. It dissolves with difficulty in ligroïn, is quite insoluble in water, but is more soluble in alcohol and ether than the corresponding monocarbamate.

Monoörthonitrocarbanilide, *o*-$NO_2C_6H_4NHCONHC_6H_5$. — When the molecular quantity of aniline dissolved in a few cc. of ether was added to an ethereal solution of *o*-nitrophenyl isocyanate, a precipitate was immediately formed which recrystallized from hot alcohol, melted at 170°. The yield was quantitative.

I. 0.1682 gram gave 0.3737 gram CO_2 and 0.0660 gram H_2O.

II. 0.1848 gram gave 27.4 cc. nitrogen at 23° and 745 mm.

	Calculated for $C_{13}H_1N_{13}O_3$.	Found.
Nitrogen	16.37	16.46
Hydrogen	4.28	4.36
Carbon	60.70	60.65

Mono-*o*-nitrocarbanilide is an almost white crystalline substance nearly insoluble in ether, ligroïn and cold alcohol, but readily soluble in hot alcohol.

Orthonitrophenylurea, *o*-$NO_2C_6H_4NHCONH_2$.—An ethereal solution of one gram of *o*-nitrophenyl isocyanate was saturated with a slow current of dry ammonia. The precipitate which formed immediately was washed with a little ether and recrystallized from hot methyl alcohol when crystals which melted at 181° were obtained.

0.1379 gram gave 28.4 cc. nitrogen at 18° and 744 mm.

	Calculated for $C_7H_7N_3O_3$.	Found.
Nitrogen	23.21	23.37

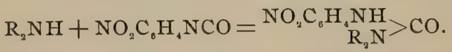
Symmetrical Orthonitrophenylorthotoluylurea, $NO_2C_6H_4NH$-$CONHC_6H_4CH_3$.—This was obtained by the action of orthotoluidine and *o*-nitrophenyl isocyanate in ethereal solution. Crystallized from alcohol it melts at 189°. In all its properties it closely resembles orthonitrocarbanilide.

0.1989 gram gave 28.6 cc. nitrogen at 26° and 745 mm.

	Calculated for $C_{14}H_{13}N_3O_3$.	Found.
Nitrogen	15.5	15.75

The Action of Dialkylated Amines on Orthonitrophenyl Isocyanates.

Dialkylated amines are added to *o*-nitrophenyl isocyanate thus:



$$R_2NH + NO_2C_6H_4NCO = \begin{matrix} NO_2C_6H_4NH \\ R_2N \end{matrix}\!>\!CO.$$

The character of the reaction is very different from that of the aromatic amines. While the latter form crystalline compounds, in the formation of which chemical action is very energetic; the former give oils and heating is necessary.

Dimethyl o-Nitrophenylurea, $(CH_3)_2NCONHC_6H_4NO_2$.—Dry dimethylamine was passed into an ethereal solution of *o*-nitrophenyl isocyanate to saturation, but a portion of the solution tested with aniline precipitated orthonitrocarbanilide, showing the presence of unchanged isocyanate. The solution was then warmed and dimethylamine passed into it till a test with aniline gave no precipitate. After the ether was driven off a yellow oil remained which became viscous at —15° and did not crystallize at —30°. This became mobile oil again at 0°. Analysis showed it to be dimethyl-*o*-nitrophenylurea.

0.1140 gram gave 20.7 cc. nitrogen at 23° and 753 mm.

	Calculated for $C_9H_{11}N_3O_3$.	Found.
Nitrogen	20.10	20.38

Diethyl-o-nitrophenylurea, $(C_2H_5)_2NCONHC_6H_4NO_2$.—This was formed by warming an ethereal solution of *o*-nitrophenyl isocyanate and diethylamine. Treating as above described for the corresponding dimethyl compound an oil was obtained which analysis showed to be diethyl-*o*-nitrophenyl urea.

0.1565 gram substance gave 25.4 cc. nitrogen at 23° and 743 mm.

	Calculated for $C_{11}H_{15}N_3O_3$.	Found.
Nitrogen	17.72	17.96

Dipropylorthonitrophenylurea, $(C_3H_7)_2NCOC_6H_5NO_2$, was formed by adding the molecular equivalent of *o*-nitrophenyl isocyanate to an ethereal solution of dipropylamine, except that reaction took place without heating. There is no difference between this and the dimethyl or diethylamine addition-products. Treated in the same way as above the urea remained as an oil.

0.2000 gram gave 29.1 cc. nitrogen at 25° and 748 mm.

	Calculated for $C_{13}H_{19}N_3O_3$.	Found.
Nitrogen	16.23	16.37

Dibutyl-o-nitrophenylurea, $(C_4H_9)_2NCONHC_6H_4NO$.—With *o*-nitrophenyl isocyanate dibutylamine behaved in exactly the same way as dipropylamine, yielding on oil which was prepared as just described.

0.1766 gram gave 23.1 cc. nitrogen at 23° and 748 mm.

	Calculated for $C_{15}H_{23}N_3O_3$.	Found.
Nitrogen	14.43	14.52

Diamyl-o-nitrophenylurea, $(C_5H_{11})NCONHC_6H_4NO_2$, was obtained from diamylamine and *o*-nitrophenyl isocyanate. Treated as above described with dipropylamine, perfectly analogous results were obtained. The resulting oil proved to be diamyl-*o*-nitrophenylurea.

0.2259 gram gave 27.4 cc. nitrogen at 25° and 746 mm.

	Calculated for $C_{17}H_{27}N_3O_3$.	Found.
Nitrogen	13.12	13.36

Chlorformparanitranilide, $NO_2C_6H_4NHCOCl$, was prepared by treating methylparanitrophenylurethane with phosphorus pentachloride in the same manner as the corresponding orthonitrophenylurethane. It yielded about 50 per cent. of the urea chloride.

0.2304 gram heated with lime gave 0.1622 gram AgCl.

	Calculated for $C_7H_6N_2O_3$.	Found.
Chlorine	17.46	17.12

Chlorform-p-nitranilide closely resembles chlorformorthonitranilide. It is almost white with a very penetrating odor, causing tears. With ethyl and methyl alcohol it gives the corresponding urethanes. With ammonia and aniline it gives ureas. Heated above 44° it loses hydrochloric acid slowly and begins to melt. At 75° it loses all its hydrochloric acid and becomes an isocyanate.

Paranitrophenyl Isocyanate, *p*-$NO_2C_6H_4NCO$.—10 grams of chlorform-*p*-nitranilide in a flask with a long delivery tube were heated for 4 hours in a current of dry air at 70°–75°. There remained in the flask a brown liquid partially soluble in ligroïn, which when cooled, deposited almost white needles in concentric clusters. After two crystallizations they melted at 44°. The substance is *p*-nitrophenyl isocyanate.

0.1902 gram gave 29.4 cc. nitrogen at 24° and 747 mm.

	Calculated for $C_7H_4N_2O_3$.	Found.
Nitrogen	17.07	17.12

Water decomposes it giving nitraniline, while amines and alcohols are added to it, forming ureas and urethanes. Standing for a long it polymerizes. Heating hastens polymerization.

Isopropyl-p-nitrophenylurethane, *p*-$NO_2C_6H_4NHCOC_3H_7$, is formed by adding isopropyl alcohol to the molecular quantity of *p*-nitrophenyl isocyanate. The yield is quantitative. The substance corresponds closely in properties to the methyl and ethyl compounds. It melts at 78°.

0.2293 gram gave 26.1 cc. nitrogen at 24° and 750 mm.

	Calculated for $C_{10}H_{12}N_2O_4$.	Found.
Nitrogen	12.5	12.66

Isobutyl-p-nitrophenylurethane, $NO_2C_6H_4NHCOC_4H_9$ is formed by the direct union of isobutyl alcohol and *p*-nitrophenyl isocyanate. The yield is quantitative. The substance melts at 62° and has properties analogous to the corresponding propylurethane.

0.2225 gram gave 23.6 cc. nitrogen at 24° and 750 mm.

	Calculated for $C_{11}H_{14}N_2O_3$.	Found.
Nitrogen	11.76	11.80

Paranitrocarbanilide, $NO_2C_6H_4NHCONHC_6H_5$. — When aniline is added to an ethereal solution of paranitrophenyl isocyanate, a precipitate is formed immediately which melts at 209° and appears to be identical with the substance described by Goldschmidt[1] (melting-point 202°), and by Leuckhart[2] (melting-point 212°).

0.2071 gram gave 30.8 cc. nitrogen at 24° and 741 mm.

	Calculated for $C_{13}H_{11}N_3O_3$.	Found.
Nitrogen	16.34	16.34

In conclusion I desire to express my sincere thanks to Professor Felix Lengfeld for the valuable assistance which he has given me in this work.

THE HYDROLYSIS OF ACID AMIDES.

By Ira Remsen.

A number of years ago, with the assistance of advanced workers in this laboratory, I carried out a series of investigations on the oxidation of substitution-products of aromatic hydrocarbons, the results of which went to show that, when the oxidizing agent is chromic acid, an oxidizable residue, situated in the ortho position with reference to an atom or group that is not oxidizable, is almost completely protected from oxidation, while similar groups in the meta or para position are easily oxidized. Later, experiments were tried on the reduction of nitro compounds of different structure, but, although results of some value were thus obtained, these have not been published, as I have hoped that the method of making the measurements might be improved. Still later, my attention was drawn to the marked difference between benzoic sulphinide (saccharin) and parasulphaminebenzoic acid[1] towards boiling dilute acids. The former is easily converted into the corresponding acid ammonium salt, while the latter remains unchanged.

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[1] Ber. d. chem. Ges., **26**, 2571.

[2] J. prakt. Chem. **41**, 322.

About a year ago I requested Mr. E. E. Reid, of this laboratory, to make some experiments on the relative ease with which the three nitrobenzamides are converted into their ammonium salts by dilute acids. Mr. Reid has since devoted himself with much skill and energy to this work, and the results reached are most interesting. A method has been devised by which it is possible to measure with a considerable degree of accuracy the rate of the hydrolysis. The experiments thus far completed have been carried out with hydrochloric acid of three concentrations and with sulphuric acid of three concentrations. The details of the experiments will be communicated later, and it will then be seen that the curves showing the rate of change are remarkably regular. A striking difference is shown in the action of the three nitrobenzamides. The following results obtained with half normal hydrochloric acid may serve as an example :

Time in hours.	Per cent. of *o*-amide changed.	Per cent. of *m*-amide changed.	Per cent. of *p*-amide changed.
½	....	21.1	24.4
1	....	42.8	48.2
1½	....	50.1	63.4
2	....	65.0	71.2
3	3.3	80.5	84.5
4	3.9	88.9	91.9
5	....	92.6	94.6
6	6.2	94.2	96.9
7	....	....	....
8	8.6	....	....

[1] See Remsen and Burton : This JOURNAL, II, 403.

The ortho amide is seen to resist the action of the hydrolysing agent to a very marked degree, so that it was difficult to measure the amount of the change if the heating was not continued for at least three hours. On the other hand, the meta and para amides yield readily, the para somewhat more so than the meta.

It seems highly probable that other aromatic acid amides that contain an atom or group in the ortho position to the group, $CONH_2$, will conduct themselves in a similar way. These phenomena are suggestive of those studied in this laboratory many years ago, to which reference has already been made. Apparently the single nitro group in the ortho position with reference to the carbamide group, $CONH_2$, *protects* this from the action of dilute acids, as the nitro group in the ortho position to methyl protects this from oxidation by chromic acid, as shown in my earlier experiments. There is also some analogy between these protection phenomena, and those recently studied by Victor Meyer and his students—an analogy which Meyer does not appear to have recognized.

The object of this note is to inform chemists that we are in possession of a method that makes measurements of the kind given above comparatively easy, and that we propose to apply the method to the study of as large a number of cases as possible, with the object of determining

(1) Whether the influence of ortho groups upon the hydrolysis of acid amides is always the same; and

(2) How various atoms and groups differ in their effect upon the rate of hydrolysis.

This work will require some time and it seems best to postpone the publication of the results until the investigation is completed.[1]

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[1] The substance of this note was communicated by me to the National Academy of Sciences, at the New York meeting held November 18, 1896.

LEHRBUCH DER ALLGEMEINEN CHEMIE. VON DR. WILHELM OSTWALD, Professor an der Universität zu Leipzig. Zweiten Bandes, zweiter Teil. Verwandtschaftslehre. Zweite umgearbeitete Auflage. Leipzig: Wilhelm Engelmann.

The first volume of this great text-book on physical chemistry, dealing with *stoichiometry*, and the first part of the second volume, treating of *thermochemistry*, *electrochemistry* and *photochemistry*, have already received notice some three years ago in this Journal.[1] The first instalment of the second part of the second and last volume has just appeared. This part will deal entirely with the question of chemical affinity in its broadest sense. The first two hundred pages, which have just come to hand, are devoted to the history of the subject. The first chapter discusses the history of chemical theories; the second, the older methods employed for determining the relative affinities of substances, together with the discussion to which the results led. In the third chapter, the more recent developments in the study of chemical affinity up to 1886, are treated historically. In this connection, the Law of Mass Action of Guldberg and Waage, the Phase Laws of J. W. Gibbs, the Studies in Chemical Dynamics by van't Hoff, and the Electrochemical Theory of Arrhenius, are especially to be mentioned. The last chapter treats of the advances which have been made since 1886, the most prominent being the van't Hoff Theory of Solutions, the Arrhenius Theory of Free Ions, the Applications of the Gas Laws to Solutions, and the Arrhenius Theory of Isohydric Solutions.

The publishers promise that this division of the *Lehrbuch* will be issued in four or five numbers, and will be completed during the coming year. A knowledge of this fact must be welcomed by all who are interested in physical chemistry, and especially by those who are called upon to teach that branch of science. For they will find here the subject of *affinity* treated in a complete and thoroughly systematic manner.

H. C. J.

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[1] This JOURNAL, **15**, 533.

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VOL. XIX. MAY, 1897. NO. 5.

AMERICAN CHEMICAL JOURNAL.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON URETHANES.

BY OTTO FOLIN.

Sodium methylate and acetbromamide in methyl alcohol solution do not yield a hydroxylamine derivative according to the following equation:

$$CH_3CONHBr + NaOCH_3 = CH_3CONHOCH_3 + NaBr;$$

but a molecular rearrangement, analogous to that observed by Hofmann[1] in the action of alkalies on acid bromamides, occurs in the course of the reaction, and a urethane is obtained in place of the isomeric hydroxylamine ether:[2]

$$CH_3CONHBr + NaOCH_3 = CH_3NHCOOCH_3 + NaBr.$$

A similar rearrangement occurs in the action of sodium methylate on paranitrobenzbromamide and on succinimide bromide.[3]

The investigations described in this paper were undertaken at the suggestion of Dr. Stieglitz and Dr. Lengfeld for the purpose of determining whether the reaction

$$RCONHBr + NaOCH_3 = RNHCOOCH_3 + NaBr$$

is general, or if it is possible to prevent the rearrangement and effect direct substitution by varying the positive and negative character of the group R.

[1] Hofmann: Ber. d. chem. Ges., **14**, 2725; **15**, 408, etc.

[2] Lengfeld and Stieglitz: This JOURNAL, **16**, 370; Stieglitz: *Ibid*, **18**, 752.

[3] This JOURNAL, **15**, 215, 504.

In the course of their investigations on urethanes, Lengfeld and Stieglitz[1] obtained chlorformanilide by the action of phosphorus pentachloride on phenylurethane:

$$C_6H_5HNCOOC_2H_5 + PCl_5 = C_6H_5NH.COCl + C_2H_5Cl + POCl_3.$$

The action of phosphorus pentachloride on substituted urethanes, as well as the action of phosphorus pentachloride and of phosgene on urethane itself was therefore made a part of this investigation in order to test the applicability of the reaction.

I. PREPARATION OF URETHANES FROM ACID BROMAMIDES.

Action of Sodium Methylate on Benzbromamide.

To the cool solution of 1.72 grams sodium in 68 grams pure anhydrous methyl alcohol was added 15 grams benzbromamide.[2] The bromide dissolved readily, but no reaction occurred in the cold. The solution was boiled on the water-bath for an hour, when a test with potassium iodide and hydrochloric acid showed that no unchanged bromamide remained. After distilling off the greater part of the alcohol, the residue was allowed to evaporate to dryness at ordinary temperatures, and the resulting product extracted with ether.

The ether extract was distilled under reduced pressure and finally recrystallized from hot water. Perfectly white crystals, melting sharply at 47°, were obtained. The compound has the composition and all the properties of methyl phenylcarbamate, $C_6H_5NHCOOCH_3$, (melting-point 47°). A synthetic preparation of the substance was identical with it in every respect; a mixture of the two melted sharply at 47°.

0.1354 gram substance gave 11.65 cc. moist nitrogen at 747 mm. and 24°.

	Calculated for $C_8H_9NO_2$.	Found.
N	9.27	9.53

The main product of the reaction is therefore methyl-phenylcarbamate. Methyl benzhydroxamate, $C_6H_5CONHOCH_3$, might, however, have been formed by direct substitution to a very slight extent as a by-product. As this substance is somewhat soluble in water, and easily soluble in ether, advantage was taken of these properties to determine whether it is formed at all by the action of sodium methylate on benzbromamide. 50 grams of the bromamide was treated as described above with the calculated amount of sodium methylate. The hard, dry mass that remained after removing the alcohol in neutral solution in a vacuum was broken up with the aid of a few drops of ether, and then extracted with water. The extract was repeatedly shaken out with ether; the ethereal solutions dried over potassium carbonate, and the ether distilled off. A small quantity of pure methyl phenylcarbamate remained; hence no methylbenzhydroxamate was formed even as a by-product. No direct replacement of the bromine atom takes place; rearrangement and formation of urethane occur quantitatively according to:

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[1] This JOURNAL, **16**, 70.

[2] Hoogewerff and Van Dorp: Rec. d. Trav. chim. d. Pays. Bas., **8**, 188.

$$C_6H_5CONHBr + NaOCH_3 = C_6H_5NHCOOCH_3 + NaBr.$$

Action of Sodium Methylate on Metanitrobenzbromamide.

Metanitrobenzbromamide was prepared as described by Hoogewerff and Van Dorf.[1] The substance when precipitated by addition of acetic acid to the alkaline solution came down in a very sticky paste. It could be washed only by taking a very small portion at a time, and it was dried on clay plates and in vacuum desiccators over sulphuric acid for seven days before it was perfectly dry.

Methyl m-Nitrophenylcarbamate, $m.NO_2C_6H_4NHCOOCH_3$.—Two grams sodium (1 atom), dissolved in 80 grams pure methyl alcohol, was heated on the water-bath with 2.15 grams *m*-nitrobenzbromamide (1 molecule) for one hour. A yellow crust formed on the sides of the flask during the heating and, on cooling, a large quantity of a yellow crystalline precipitate was formed. The substance was identified as *m*-nitrophenylmethylurethane. After removing the precipitate by filtration most of the alcohol was distilled off. The mixture changes in color and decomposes on prolonged heating, and the evaporation was, therefore, completed at ordinary temperatures. The residue was extracted with chloroform, and the extract gave by recrystallization from warm chloroform well-formed octahedrons, melting at 147°–149°. The compound is *methyl metanitrophenylcarbamate*, *m*-$NO_2C_6H_4NHCOOCH_3$, and is obtained in quantities corresponding to 90 per cent. of the theoretical.

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[1] Rec. trav. chim., 8, 193.

0.1153 gram substance gave 15.2 cc. moist nitrogen (over 30 per cent. caustic potash) at 743 mm. and at 22°.

	Calculated for $C_8H_8N_2O_4$.	Found.
N	14.28	14.66

Methyl metanitrophenylcarbamate, not being known, was prepared synthetically from *m*-nitraniline and methyl chlorformate. It was identical with the body just described.

Action of Sodium Methylate on Orthonitrobenzbromamide.

o-Nitrobenzbromamide has also been prepared by Hoogewerff and Van Dorp.[1] The compound is not so pasty as the meta derivative and can be washed and dried very rapidly.

Methyl-o-Nitrophenylcarbamate, *o*-$NO_2C_6H_4NHCOOCH_3$.—10.5 grams *o*-nitrobenzbromamide was added to 1 gram of sodium dissolved in 40 grams methyl alcohol. It dissolved, but no noticeable reaction took place in the cold. The mixture was then heated on the water-bath for twenty minutes. At the end of this time there was no unchanged bromamide left in the solution. The slightly alkaline solution was then acidified with a few drops of dilute acetic acid, and the alcohol allowed to evaporate at ordinary temperatures. The residue, extracted ten times with boiling (40°–50°) ligroïn, gave about 7 grams of a dark yellow oil which, on cooling, solidified. This substance is methyl *o*-nitrophenylcarbamate, mixed with a small quantity of *o*-nitraniline. To remove the latter the mixture was dissolved in pure, cold chloroform and *o*-nitraniline hydrochloride precipitated by means of dry hydrochloric acid gas. The urethane was then precipitated with ligroïn and, after repeated recrystallization from ligroïn, its melting-point was found constant at 53°. *o*-Nitrophenylurethane consists of well-formed greenish-yellow crystals, and is quite soluble in all the ordinary organic solvents except low-boiling ligroïn.

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[1] Rec. trav. chim., **8**, 191.

0.2977 gram substance gave 0.5383 gram CO_2 and 0.1192 gram H_2O.

	Calculated for $C_8H_8N_2O_4$.	Found.
C	48.98	49.31
H	4.08	4.45

In order to obtain the yield of urethane indicated above (90 per cent.) it is essential that the experiment should be performed as described. As soon as heat is applied to the alcoholic solution of sodium methylate and *o*-nitrobenzbromamide, it turns red and the color deepens as the heating is continued, until at the end of about one hour it is found that the chief product is *o*-nitraniline, most of the urethane evidently being saponified.

As methyl *o*-nitrophenylcarbamate is comparatively unstable at higher temperatures, I attempted to complete the reaction at a temperature below that of boiling methyl alcohol. At 50° I found that the reaction goes about the same as at 66°–70°, and the relative amount of each of the various products obtained varies with the time the heating is continued. At 30°, on the other hand, the result is somewhat different. The reaction proceeded very slowly and was not completed at the end of the fifth hour. The solution remained clear at first, but after a couple of hours, a precipitate, consisting of small white crystals, appeared. This increased constantly in amount until it was removed by filtration at the end of five hours, after which the reaction was completed by boiling on the water-bath for fifteen minutes. The precipitate melted at 220°. It is insoluble in all the ordinary organic solvents except acetone. The same compound was obtained in larger quantities by Swartz,[1] who also made a closer investigation of it, and by analysis and synthesis showed it to be *o*-nitrophenyl-*o*-nitrobenzoylurea,

$$(o)\text{-}NO_2C_6H_4NHCONHCOC_6H_4NO_2\text{-}(o).$$

The substance obtained in this reaction is in every respect identical with the synthetic product prepared by Swartz. Its formation here is due to the reducing action of methyl alcohol on a part of the *o*-nitrobenzbromamide, giving formaldehyde and

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[1] See This Journal, **19**, 295.

o-nitrobenzamide, the latter of which is then acted upon by a molecule of *o*-nitrophenyl isocyanate, formed by the rearrangement of a second molecule of *o*-nitrobenzbromamide.[1] The odor of the aldehyde was quite distinct.

1. $NO_2C_6H_4CONHBr + NaOCH_3 = NO_2C_6H_4CONH_2 + CH_2O + NaBr.$
2. $NO_2C_6H_4CONHBr + NaOCH_3 = NO_2C_6H_4N{=}CO + NaBr + HOCH_3.$
3. $NO_2C_6H_4N = CO + NH_2COC_6H_4NO_2 = NO_2C_6H_4NHCONHCOC_6H_4NO_2.$

Action of Sodium Methylate on Metabrombenzbromamide.

Pure *m*-brombenzoic acid was converted successively with phosphorus pentachloride and ammonia into the acid chloride and *m*-brombenzamide. The latter crude product was not perfectly white, but it was quite pure and had a melting-point somewhat higher than that found by Engler,[2] 150°. Recrystallized from chloroform, it was obtained in perfectly white crystals, melting at 153°–4°. Analysis showed its purity:

0.2014 gram substance gave 12.6 cc. moist nitrogen at 740.3 mm. and 21°.

	Calculated for C_7H_6NOBr.	Found.
N	7.00	6.97

Metabrombenzbromamide, *m*-$BrC_6H_4CONHBr$.—This bromide was not known; but it was prepared from the amide by exactly the same method as that used by Hoogewerff and Van Dorp in the preparation of the nitrobenzbromamides. The yield was good. The compound was slightly colored and consisted of prismatic, microscopic needles, melting at 105°. The bromine attached to the nitrogen was determined in the crude product, and no attempt was made to obtain it in perfectly pure condition:

	Calculated for $(C_7H_5BrON)Br$.	Found.
Active bromine	28.7	27.9

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[1] Hofmann: Ber. d. chem. Ges., **14**, 2725; Lengfeld and Stieglitz: This JOURNAL, **15**, 506: Stieglitz: *Ibid*, **18**, 752.

[2] Ber. d. chem. Ges., **4**, 708.

Methyl Metabromphenylcarbamate, m-$BrC_6H_4NHCOOCH_3$.—Five grams *m*-brombenzbromamide was added to 0.4 gram sodium dissolved in 20 grams absolute methyl alcohol, and the mixture heated for one hour. The solution was neutralized and the greater part of the alcohol distilled off. On adding water to the remainder, a white precipitate came down. This was recrystallized from chloroform by the addition of ligroïn and analyzed.

0.2678 gram substance gave 15.25 cc. moist nitrogen at 749.3 mm. and 25°.

	Calculated for $C_8H_8NO_2Br$.	Found.
N	6.09	6.29

Methyl *m*-bromphenylcarbamate is a white crystalline compound melting at 84.5°–85.5°; insoluble in water and soluble in all the ordinary organic solvents except ligroïn. The yield of urethane in the above reaction is from 80 to 90 per cent. of the theoretical, and the remainder of the bromamide is reduced to the amide and is recovered.

As the work just described shows that the rearrangement of the acid bromamides, RCONHBr, occurs almost quantitatively, even when R is strongly negative ($R = C_6H_5$; o-$NO_2C_6H_4$; m-$NO_2C_6H_4$; m-BrC_6H_4), the effect of positive radicals was studied. A dialkylamidobenzamide, $R_2NC_6H_4CONH_2$, was first chosen rather than an amidobenzamide in order to remove the possibility of the hypobromite acting on the amide group attached to the benzene ring, in preparing the bromamide. As no such amides had been prepared and described, a few experiments were first made to determine the best method for obtaining them.

p-Diethylamidobenzamide, p-$(C_2H_5)_2NC_6H_4CONH_2$.—Michler obtained dimethylamidobenzoic acid by heating dimethylaniline and phosgene in sealed tubes to 50° and pouring the resulting mixture into water.[1] To prepare the amide 62 grams phosgene was passed into 95 grams diethylaniline in a flask attached to an inverted condenser cooled with a freezing-mixture. The two reacted slowly, the mixture gradually solidifying to a white mass, which was colored first red and later a deep blue:

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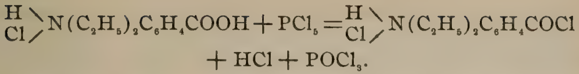
[1] Ber. d. chem. Ges., 9, 400, etc.

$$(C_2H_5)_2NC_6H_5 + COCl_2 = (C_2H_5)_2NC_6H_4COCl + HCl.$$

The crude chloride thus formed was slowly added to an excess of strong, cold ammonia. The reaction was quite violent; but only 12 grams of the expected acid amide was obtained, the greater portion of the acid chloride being converted into diethylamidobenzoic acid instead. The amide obtained in this reaction is not pure. It is mixed with benzophenone derivatives, and a blue coloring matter, which can be removed only very slowly and with great loss by fractional precipitation from hot alcohol.

Since diethylamidobenzoic acid is easily purified, it was thought best first to prepare this pure, and then convert it by means of phosphorus pentachloride and ammonia into the amide. The acid was prepared by Michler's method and purified by dissolving in alkalies and reprecipitating the acid with acetic acid (melting-point 188°).

Action of Phosphorus Pentachloride on p-Diethylamidobenzoic Acid.—Phosphorus pentachloride and diethylamidobenzoic acid were mixed in molecular quantities. Action set in only with great difficulty at 60°–70°, and the mass became very brown as the reaction proceeded. The amide obtained by the action of ammonia on this product was quite impure. A very smooth reaction can be brought about by first passing dry hydrochloric acid into a chloroform solution of diethylamidobenzoic acid, thus converting it into the hydrochloride, $HCl(C_2H_5)_2NC_6H_4COOH$, before adding phosphorus pentachloride. Reaction with the latter now sets in at once at 40°–50°, a clear, colorless mixture of phosphorus oxychloride and the hydrochloride of diethylamidobenzoic acid chloride being obtained. This behavior of diethylamidobenzoic acid toward phosphorus pentachloride is further evidence that it is really a salt, perhaps $H\underbrace{N(C_2H_5)_2C_6H_4COO}$, which like other salts, would not react so readily with phosphorus pentachloride. The hydrochloride, $ClHN(C_2H_5)_2C_6H_4COOH$, is a true acid and reacts as smoothly with phosphorus pentachloride as any other acid:



$$\left.\begin{matrix}H\\Cl\end{matrix}\right\rangle N(C_2H_5)_2C_6H_4COOH + PCl_5 = \left.\begin{matrix}H\\Cl\end{matrix}\right\rangle N(C_2H_5)_2C_6H_4COCl + HCl + POCl_3.$$

The acid chloride thus obtained gives, with ammonia, diethylamidobenzamide in very pure condition, with a yield of 50 per cent. Considerable quantities of regenerated acid were always recovered from the ammoniacal filtrate, with only slight loss of material.

p-Diethylamidobenzamide is a white crystalline solid melting at 136°–137°. It is readily soluble in hot water and in hot alcohol, but is very little soluble in any of the other organic solvents.

0.1878 gram substance gave 24.2 cc. moist nitrogen at 740 mm. and 17°.

	Calculated for $C_{11}H_{16}N_2O$.	Found.
N	14.58	14.61

Ethyl Diethylamidobenzoate, $(C_2H_5)_2NC_6H_4COOC_2H_5$. — In place of converting diethylamidobenzoic acid into the amide by means of its chloride, an attempt was made to prepare it from its ester. The best yield of ethyl diethylamidobenzoate (75 per cent.) was obtained by dissolving the acid in alcohol and heating it with from 4 to 5 equivalents of sulphuric acid on the water-bath for ten hours. Ethyl diethylamidobenzoate is described by Michael and Wing as an oil which solidifies in a freezing-mixture, but melts again at ordinary temperatures.[1] I found it to be a white solid consisting of irregular rhombohedral plates, insoluble in water and very soluble in ether and chloroform. It was repeatedly recrystallized from hot alcohol until it melted sharply at 43°.

0.2942 gram substance gave 0.7616 gram CO_2 and 0.2464 gram H_2O.

	Calculated for $C_{13}H_{19}NO_2$.	Found.
C	70.60	70.59
H	8.6	9.31

Ethyl Diethylamidobenzoate and Ammonia.—From the ester thus prepared I was unable to get the corresponding amide by treatment with ammonia. The ethyl diethylamidobenzoate was heated with a large excess of aqueous ammonia and with alcoholic ammonia on the water-bath; it was left in glass-stoppered bottles with concentrated aqueous ammonia and with saturated alcoholic ammonia for several weeks, but not a trace of the acid amide was obtained. The ester remained unchanged.

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[1] This JOURNAL, 7, 197.

The yield of diethylamidobenzamide obtained from diethylaniline by way of diethylamidobenzoic acid being rather unsatisfactory, a better yield of such an amide was sought by converting dimethylaniline into an amide by means of the nitrile, $(CH_3)_2NC_6H_4CN$.

Action of Cyanogen Bromide on Dimethylaniline.—As the hydrogen atom in the para position to the amide group in dimethylaniline is very easily replaced, the latter might, it seemed, be converted by the action of cyanogen bromide into dimethylamidobenzonitrile. Dimethylaniline in dry chloroform solution was first converted into its hydrochloride and mixed with one molecule of cyanogen bromide. Aluminium chloride was then added, a small portion at a time; it produced a lively reaction in the mixture. All but the aluminium chloride went into solution. The latter was removed by filtration; the filtrate distilled, and the solid residue distilled with steam. A crystalline solid came over, which was soluble in all the organic solvents and melted at 55°–56°. The melting-point and all the properties of the compound correspond to those of parabromdimethylaniline. It was prepared synthetically and the two were identical.

The reaction, therefore, did not take place as was expected and the bromine, instead of the cyanogen radical, was found to have replaced the para hydrogen atom in dimethylaniline.

$$(CH_3)_2NC_6H_4H + BrCN = (CH_3)_2NC_6H_4Br + HCN.$$

Action of Cyanogen Bromide on Parabromdimethylaniline.—Cyanogen bromide failing to give the nitrile by acting on dimethylaniline, its action on *p*-bromdimethylaniline in the presence of sodium was tried, in the attempt to fulfil the equation:[1]

$$(CH_3)_2NC_6H_4Br + 2Na + BrCN = (CH_3)_2NC_6H_4CN + 2NaBr.$$

[1] Claus: Ber. d. chem. Ges., **16**, 915.

2.75 grams sodium wire in 100 grams absolute ether was cooled in a freezing-mixture. 12 grams *p*-bromdimethylaniline[1] and 6.26 grams cyanogen bromide were mixed and added to the sodium in the ether.

Both bodies dissolved in the ether, but no reaction took place until the flask was taken out of the freezing-mixture. The reaction was very rapid, as the contents of the flask began to get a little warmer, but was easily regulated by cooling. After the reaction was completed, a solid containing only sodium bromide and sodium cyanide was removed by filtration and the ether distilled off. The remaining residue was found to be only unchanged *p*-bromdimethylaniline. The cyanogen bromide, therefore, is decomposed by the sodium and no nitrile is obtained.

p-Dimethylamidobenzonitril, *p*-$(CH_3)_2NC_6H_4CN$.—By treating the diazochloride of *p*-amidodimethylaniline with Sandmeyer's potassium cyanide-copper sulphate solution, Ahrens[2] obtained an oil from which he was unable to isolate the nitrile, but which gave dimethylamidobenzoic acid with alcoholic potash, proving the presence of the nitrile. No statement of the yield being made, Ahrens' work was repeated by me.

The oil described by him was obtained, and was distilled with steam. At first a colorless oil came over which was found to be dimethylaniline. Afterwards a light-colored substance was carried over, which solidified in the condenser. It was purified by precipitating it from ether solution with ligroïn, and thus obtained in slightly yellowish needles, which melted at 74°–76°. It is very soluble in chloroform and ether, and very little soluble in low-boiling ligroïn. By prolonged boiling with strong alcoholic potash it is converted into *p*-dimethylamidobenzoic acid (melting-point [illegible]°). Its properties show it to be *p*-dimethylamidobenzonitrile, but the yield was too small to make its preparation an advantageous one for the purpose of obtaining a dialkylamidobenzamide. These are therefore best prepared from the dialkylamidobenzoic acids by the successive action of hydrochloric acid, phosphorus pentachloride, and ammonia, as described above.

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[1] Weber: Ber. d. chem. Ges., **8**, 715; **10**, 763.

[2] Ber. d. chem. Ges., **20**, 2958.

Action of Potassium Hypobromite on p-Diethylamidobenzamide.—One gram diethylamidobenzamide was added to a cold solution containing the calculated quantity of potassium hypobromite. A part of the amide dissolved, and a precipitate was formed which quickly changed to a dark-brown color. The solution was filtered and cold boric acid added to the filtrate. A brown sticky precipitate resembling the first one was thrown down. It dissolved in hydrochloric acid and was again precipitated with ammonia; but it did not give off bromine with the acid or nitrogen with ammonia. The dry substance gave a very distinct dark green flame when ignited with copper oxide, and was probably some compound containing one or more bromine atoms in the benzene ring. It certainly was not diethylamidobenzbromamide, $(C_2H_5)_2NC_6H_4$ CONHBr. As acid chloramides are rather more stable than the corresponding bromamides, diethylamidobenzamide was allowed to react with molecular quantities and with excess of hypochlorous acid. A yellow, sticky precipitate was extracted with ether, and a substance obtained which gave the test for halogen amide with potassium iodide and hydrochloric acid when freshly prepared; but it rapidly decomposed, and when left over night it no longer gave the test for halogen amide. On account of this instability of the halogen amides, $R_2NC_6H_4CONHX$, the action of sodium methylate on them could not be investigated.

Action of Hypobromite on Metamidobenzamide.—Another attempt was made with metamidobenzamide. This amide was treated with cold potassium hypobromite solution in the usual manner. A reddish precipitate was obtained which, when placed on clay plates, soon turned to a black amorphous mass containing bromine and not melting below 280°. The experiment was repeated in various ways, but with no better results. The black amorphous mass was extracted with ether, alcohol and chlorform in a Soxhlet apparatus; but each extract was amorphous, and no definite product was isolated. Several of these extracts, as well as the residue, were heated in sealed tubes with hydrochloric acid and the products examined for metaphenylenediamine, but none was found.

Having thus failed to obtain an acid bromamide containing the amido or dialkylamido groups in the benzene ring, probably on account of the remarkable reactivity which such positive groups give to the benzene ring, I succeeded in preparing an analogous acid bromamide in the aliphatic series, on which the action of sodium methylate was tried. Carbomethoxy-β-amidopropionamide, $CH_3O_2CNHCH_2CH_2CONH_2$, was selected because it can be prepared without much difficulty.[1]

Carbomethoxy-β-amidopropionbromamide, $CH_3O_2CNHCH_2$-$CH_2CONHBr$.—Two grams caustic potash was dissolved in a very small quantitity of water, and 2.1 grams bromide added at —5°, and to this cold solution was added 2 grams carbomethoxy-β-amidopropionamide. The latter dissolved in a few minutes. Cold acetic acid was next added in slight excess without letting the temperature of the mixture rise above —5°. The acetic acid does not precipitate the bromamide at once, as it does in the precipitation of the aromatic ones; but in a few minutes the precipitate begins to form and then comes down very rapidly. The yellow crystalline bromamide was rapidly filtered and washed with a small quantity of cold water. It is easily soluble in water and no attempt was made to obtain it in perfectly pure condition. By using very small quantities of cold water a good yield of bromamide (80 per cent. pure) was obtained. Crude carbomethoxy-β-amidopropionbromamide is a white crystalline compound and melts with decomposition at 117°–118°.

Action of Sodium Methylate on Carbomethoxy-β-amidopropionbromamide.

0.4 gram sodium was dissolved in 20 grams absolute methyl alcohol and 4.5 grams carbomethoxy-β-amidopropionbromamide added. The latter dissolved and the mixture was boiled half an hour, when no bromamide was left unchanged. The solution was carefully neutralized with acetic acid and the mixture allowed to evaporate to dryness in a vacuum-desiccator. The white solid mass that remained was extracted with chloroform, and the chloroform solution washed with small quantities of dilute hydrochloric acid, caustic soda solution and water. The solution was then dried over calcium chloride, and the chloroform distilled. An oil remained which solidified as soon as it began to cool. The weight of this solid was only 0.3 gram. Some was undoubtedly removed by the repeated washings of the chloroform solution; but the main object sought was purity of substance rather than a larger yield. It was recrystallized from dilute alcohol and from water, giving 0.2 gram of a compound melting at 132°–3°. The melting-point, crystalline form and solubilities of this compound are the same as those ascribed by Franchimont and Klobbie[1] to the dimethyl ester of ethylenedicarbamic acid, $CH_3O_2CNHCH_2CH_2NHCO_2CH_3$.

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[1] Lengfeld and Stieglitz: This JOURNAL, 15, 512.

0.1484 gram substance gave 22 cc. moist nitrogen at 744 mm. at 24°.

	Calculated for $C_6H_{12}N_2O_4$.	Found.
N	15.91	16.35

The usual rearrangement,

$$CH_3O_2CNHCH_2CH_2CONHBr + NaOCH_3 = CH_3O_2CNHCH_2CH_2NHCO_2CH_3 + NaBr,$$

occurs, therefore, in this case; but exactly what yield of urethane can be obtained, or what other products are formed, was not investigated on account of the small amount of material on hand.

The above experiments show that the reaction,

$$RCONHBr + NaOCH_3 = RNHCOOCH_3 + NaBr,$$

is quite general, as it succeeded with all acid bromamides that could be isolated and investigated.

II. ACTION OF PHOSPHORUS PENTACHLORIDE ON URETHANES.

Action of Phosphorus Pentachloride on Phenylurethane.

Lengfeld and Stieglitz[2] obtained, by the action of phosphorus pentachloride on 10 grams phenylurethane, about 3 grams chlorformanilide,

$$C_6H_5NHCOOC_2H_5 + PCl_5 = C_6H_5NHCOCl + C_2H_5Cl + POCl_3.$$

The chief reason why a larger yield was not obtained seems to be that a part of the chlorformanilide at the temperature of the reaction (50°–60°) lost hydrochloric acid giving phenyl isocyanate, which is quite soluble in ligroïn.[1] The reaction of phosphorus pentachloride and phenylurethane was repeated under somewhat different conditions to improve the yield.

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[1] Rec. d. trav. chim. Phys. Bas., 7, 258.

[2] This Journal, 15, 71.

6.25 grams phosphorus pentachloride and 5 grams urethane gave 1.5 grams chlorformanilide after removing the phosphorus oxychloride with ligroïn (boiling-point 40°–60°). The mixed liquids were transferred from the solid precipitate into another flask and dry hydrochloric acid was then passed through the mixture. In a few minutes crystals began to appear. The current of hydrochloric acid was continued for about half an hour, the ligroïn being renewed from time to time. 0.8 gram chlorformanilide was thus obtained, increasing the yield, therefore, over fifty per cent. The best conditions for preparing chlorformanilide were found to be as follows:

10 grams urethane was acted upon by 12.5 grams phosphorus pentachloride. Pure, dry chloroform was then added in small quantity, and hydrochloric acid gas passed through the solution at ordinary temperatures until nearly all the phosphorus oxychloride had been driven off, the chloroform being renewed as fast as it was removed. The dissociation into the volatile isocyanate and hydrochloric acid is diminished by the stream of hydrochloric acid gas, and chlorformanilide, not being volatile at ordinary temperatures, remains. The latter was then precipitated as before by the addition of low-boiling ligroïn and nearly 6 grams, or about 60 per cent. of the theoretical yield, was obtained, which is almost twice as much as was obtained without the addition of dry hydrochloric acid.

Action of Phosphorus Pentachloride on Metanitrophenylurethane.

8.5 grams *m*-nitrophenylurethane and 8.5 grams phosphorus pentachloride were heated together in a dry flask to 55°–65°. No reaction took place until some of the urethane was brought into solution by the addition of a little dry chloroform. The reaction-product was cooled in a freezing-mixture and dry hydrochloric acid passed through. In a few minutes a white crystalline solid appeared, and increased rapidly until the whole of the contents in the flask solidified. More chloroform was added, and was driven off by a continuous, strong stream of hydrochloric acid, in order to carry off most of the phosphorus oxychloride. Cold ligroïn was added and the precipitate rapidly filtered and washed. 6.6 grams *m*-nitrophenylurea chloride or 81 per cent. of the theoretical yield was obtained. Chlorformmetanitranilide is a nearly colorless crystalline solid, which melts at 102° with decomposition.

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[1] Werner: Ber. d. chem. Ges., **26**, 1565; Hentchel: *Ibid*, **18**, 1178.

I. 0.2956 gram substance gave 0.04895 gram chlorine.

II. 0.2877 gram substance gave 0.04772 gram chlorine (Volhard).

	Calculated for $C_7H_5N_2O_3Cl$.	Found. I.	II.
Cl	17.72	16.56	16.59

Urea chlorides decompose readily, losing hydrochloric acid, and hence the figures are low.

Metanitrophenylurea, *m*-$NO_2C_6H_4NHCONH_2$. — In order more fully to identify the urea chloride obtained in the last experiment, a small amount of it was added to ammonia. It reacted violently, and a yellow crystalline solid was formed, which after recrystallization from hot water, melted at 195°, with slight decomposition. Hofmann[1] describes *m*-nitrophenylurea as consisting of long yellow needles. If the hot water solution is allowed to cool very slowly the substance does come down as described by Hofmann; but if rapidly cooled, it comes down in plates.

0.1788 gram substance gave 36 cc. moist nitrogen at 746 mm. and 19°.

	Calculated for $C_7H_7N_3O_3$.	Found.
N	23.20	23.06

Metanitrophenyl Isocyanate, *m*-$NO_2C_6H_4NCO$.—Metanitrophenylurea chloride was heated in a current of dry air to 110°–140° until no trace of hydrochloric acid could be detected in the air that had passed through the apparatus. The residue was then extracted with sodium-dried ligroïn. The isocyanate is quite soluble in boiling ligroïn, and on cooling it comes down as a microcrystalline, inodorous, white solid, melting at 49°–50°.

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[1] Ann. Chem. (Liebig), **67**, 156; **70**, 137.

0.1957 gram substance gave 30.9 cc. moist nitrogen at 741 mm. and 23°.

	Calculated for $C_7H_4N_2O_3$.	Found.
N	17.08	17.33

Metanitrophenyl isocyanate has all the characteristics of phenyl isocyanate, except the odor, and readily gives the usual isocyanate addition-products. Methylnitrophenylurethane, m-$NO_2C_6H_4NHCOOCH_3$, (melting-point 148°) was obtained by the action of isocyanate on absolute methyl alcohol. The corresponding ethylurethane[1] (melting-point 63°) was similarly obtained from ethyl alcohol. With ammonia the reaction is very violent, giving the *m*-nitromonophenylurea just described above.

Metanitrophenyl-m-nitrobenzoylurea, m-$NO_2C_6H_4NHCONH$-$COC_6H_4NO_2$-m.—Molecular quantities of metanitrophenyl isocyanate and *m*-nitrobenzamide were heated to 150°. The melted mixture soon solidified and the product was found to be *m*-nitrophenyl-*m*-nitrobenzoylurea, melting at 230°.

$$m\text{-}NO_2C_6H_4NCO + H_2NOCC_6H_4NO_2\text{-}m = NO_2C_6H_4NHCONHCOC_6H_4NO_2\text{-}m.$$

This urea is isomeric with the corresponding ortho derivative obtained by me as a by-product in the action of sodium methylate on orthonitrobenzbromamide.

0.1577 gram substance gave 24.9 cc. moist nitrogen at 740 mm. and 24°.

	Calculated for $C_{14}H_{10}N_4O_6$.	Found.
N	16.97	17.32

Action of Phosphorus Pentachloride on Metabromphenylurethane.

Metabromphenylurethane reacted with phosphorus pentachloride quite as readily as did the *m*-nitrophenylurethane and a good yield of white, crystalline *m*-bromphenylurea chloride, m--$BrC_6H_4NHCOCl$, was obtained.

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[1] Struve und Radenhausen: J. prakt. Chem., **52**, 230. They give the melting-point 56°. Swartz: This JOURNAL, **19**, 295, found the melting-point 65°.

The compound was identified by treating it with strong ammonia thus producing

Metabromphenylurea, *m*- $BrC_6H_4NHCONH_2$. — *m*-Bromphenylurea is very little soluble in all the ordinary organic solvents except alcohol. It was purified by dissolving an absolute alcohol and precipitating with ether and ligroïn. White needles, softening at 162°, melting at 164°–5°.

0.1514 gram substance gave 18.15 cc. moist nitrogen at 742 mm. and 25.3°.

	Calculated for $C_7H_7N_2OBr$.	Found.
N	13.02	13.12

These experiments show that with urethanes of the aromatic amines the reaction,

$$RNHCOOCH_3 + PCl_5 = RNHCOCl + CH_3Cl + POCl_3,$$

is general. Methyl chloride is first split off, giving chlorformanilides which are easily isolated, and from which the isocyanates can readily be obtained by the further loss of hydrochloric acid.

Phenyl isocyanate and chlorformanilide, hitherto prepared from aniline and phosgene, can be more conveniently prepared, especially in moderate quantities, by the method just described.[1] And since metanitrobenzoic acid is easily available, and can be readily converted into methyl *m*-nitrophenylcarbamate and its chloride, the latter may often be conveniently used in place of phenyl isocyanate, the melting-points of its derivatives being 15° to 100° higher.

Whether the above reaction is also applicable to the urethanes of the aliphatic amines and to urethane itself remained to be ascertained. I have studied the action of phosphorus pentachloride on urethane.

Preparation of Urethane.

Liebig and Wöhler[2] passed isocyanic vapors into a mixture of alcohol and ether and obtained in addition to allophanic ethylester small quantities of urethane. The use of potassium isocyanate and hydrochloric acid in place of the isocyanic acid vapors for the preparation of urethane seems never to have been tried. Amato[1] obtained allophanic ether from such a mixture of potassium isocyanate, alcohol, and dilute hydrochloric acid by boiling two days.

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[1] In making the urethanes it is not necessary to isolate the bromamides. As has been found by Miss Jeffreys, working under the direction of Dr. Stieglitz, a mixture of the acid amide and bromine dissolved in methyl alcohol may be treated with the solution of sodium methylate, or bromine may be added to such a solution of the amide and the methylate. In this way the urethanes can be prepared from many acid amides in good yield in one to two hours. Miss Jeffreys will report later on this reaction in this JOURNAL.

[2] Ann. Chem. (Liebig), **54**, 370; **58**, 260.

A good yield of urethane can nevertheless be obtained from just such a mixture by proceeding as follows: 5 grams potassium isocyanate was dissolved in just enough dilute (50 per cent.) warm alcohol to make a clear solution. This was then slowly added to a strong alcoholic solution of hydrochloric acid containing an excess of acid. The reaction is completed only very slowly on account of the insolubility of potassium isocyanate in alcohol, and the mixture was left standing at ordinary temperatures till the following day. A white precipitate was formed when the two solutions were mixed, and after twenty-four hours it gave off no gas when treated with aqueous hydrochloric acid. The excess of hydrochloric acid was neutralized with barium carbonate, the mixture filtered, and most of the alcohol removed by distillation. The remainder was allowed to evaporate to dryness in a vacuum-desiccator. The residue, extracted with ether, gave, after drying and distilling off the ether, 3.3 grams urethane, corresponding to a yield of 60 per cent. Urethane is quite volatile, and it was found by experiment that a considerable quantity is carried over by the alcohol when the latter is removed by distillation. Such losses could undoubtedly be avoided, and the above yield largely increased by using a Hempel tube in distilling off the alcohol.

Action of Phosphorus Pentachloride on Urethane.

10 grams (1 molecule) urethane and 23.3 grams phosphorus pentachloride (1 molecule) were mixed and at once began to react with evolution of a considerable amount of gas and with the absorption of so much heat that the flask containing the mixture became quite cold. In twenty minutes the reaction seemed to be complete, leaving a clear, colorless liquid in the

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[1] Jsb. d. Chem., *1873*, 749.

flask. Gattermann,[1] who prepared carbamic acid chloride, NH_2COCl, by the action of phosgene on ammonium chloride describes it as a white, crystalline body, insoluble in ligroïn, melting at 50° and boiling at 61°–62°. Dry ligroïn produced, however, no precipitate in the above liquid, even when cooled in a freezing-mixture. The ligroïn solution was slowly added to cold aniline, and the resulting white, solid mixture carefully examined for monophenylurea, but none was found.

The gas given off in the cold consists chiefly of hydrogen chloride but, on heating, much ethyl chloride escapes. The reaction was repeated in a current of dry hydrogen chloride, and the mixture distilled at 40 mm. in a current of hydrogen chloride, which was intended to decrease possible loss of chlorformamide by dissociation.[2] The distillate was collected in several different fractions, each of which reacted violently with water, giving carbon dioxide in quantities of only 44 to 66 per cent. of the theoretical for chlorformamide. With aniline no phenylurea could be obtained, with methyl alcohol no methylurethane, all of which experiments show that by the action of phosphorus pentachloride on urethane, unlike that on phenylurethane, no chlorformamide is formed. A final effort to show its presence was based on the fact that chlorformamide very readily gives with urethane ethyl allophanate,[3] which is easily isolated and recognized. A portion of the distillate mentioned was added to an ethereal solution of urethane. No reaction took place until after the ether had been distilled off and the heating on the water-bath continued for ten minutes. After the evolution of hydrochloric acid, which further heating produced, had ceased, the mixture solidified on cooling. This solid, washed and dried, melted at 190°. After recrystallization it was analyzed and found to be ethyl allophanate.

0.2420 gram substance gave 47 cc. moist nitrogen at 742 mm. and 24.5°

	Calculated for $C_4H_8N_2O_3$.	Found.
N	21.21	21.30

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[1] Ann. Chem. (Liebig), **244**, 29.

[2] Gattermann : *Ibid.*

[3] Gattermann : *Ibid.*

As Schroeter and Livinsk[1] had attempted to prepare allophanic ether by the action of phosphorus oxychloride on urethane, and had found that none was formed, it seemed here that the formation of allophanic ether must have been due to the presence of chlorformamide in the above distillate. It was thought best, however, to repeat the work of Schroeter and Livinsk and, on heating molecular quantities of urethane and phosphorus oxychloride on the water-bath, I obtained quite different results from those published by these chemists. Hydrochloric acid soon began to come off, and, on removing the unchanged urethane and phosphorus oxychloride with water, a residue remained from which allophanic ether was obtained and identified as usual.

The formation of allophanic ether in the action of urethane on the unknown chloride obtained by distilling a mixture of urethane and phosphorus pentachloride does, therefore, not prove the presence of chlorformamide in the distillate, while the other experiments described leave little doubt that no chlorformamide is formed in the reaction. From the results of a study of the action of phosgene on urethane, which will presently be described, and which showed the amide group in urethane to be most sensitive to reaction, it seems probable that when phosphorus pentachloride acts on urethane, besides forming as with other urethanes the chlorformamide complex, it introduces at the same time a phosphoric acid radical into the amide group, giving derivatives of the nature of, *e. g.*, $Cl_2P(NHCOCl)_3$ or $Cl_2PO(NHCOCl)$, etc. Such substances would give carbon dioxide with water, (40–70 per cent. as much as an equal weight of chlorformamide) and would give no phenylurea with aniline, nor urethane with alcohol.

III. ACTION OF PHOSGENE ON URETHANE.

One of the chief difficulties encountered in the study of the action of phosphorus pentachloride on urethane being the removal of phosphorus oxychloride from the reaction-product, phosgene, which has been used in similar cases[2] in place of phosphorus pentachloride because it gives only gaseous by-products, was brought into action with urethane. Its action on urethane might be analogous to the action of phosphorus pentachloride on phenylurethane, and thus give chlorformamide:

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[1] Ber. d. chem. Ges., **26**, 2171.

[2] Kempf: J. prakt. Chem. [2], **1**, 402.

$$NH_2COOC_2H_5 + COCl_2 = NH_2COCl + CO_2 + C_2H_5Cl.$$

The only previous work[1] done on the action of phosgene on urethane rather indicated that such is the primary reaction. Loeb obtained from phosgene in benzene solution and a large excess of urethane, allophanic ether, as sole product, the very substance which chlorformamide forms in presence of an excess of urethane.[2]

Loeb, in the brief notice he published on the reaction, suggested that the allophanic ether could be formed by abstracting one molecule of alcohol from two molecules of urethane without indicating in what way such a reaction might take place. He also suggested another explanation for the formation of allophanic ether; *viz.*, that it might be a decomposition-product of a hypothetical intermediate substance, carbonyl diurethane, $CO(NHCOOC_2H_5)_2$, which was not obtained, but which he supposed might have been formed and then been decomposed by recrystallization from alcohol or chloroform, losing alcohol and carbon dioxide, and giving allophanic ether.

I varied the conditions of Loeb's reaction somewhat, using undiluted phosgene, and, in order to fulfil the above equation, equal molecules of phosgene and urethane were brought into action. 5 grams phosgene and 4 grams urethane were heated in a sealed tube to 75° for half an hour. When the tube was opened the escaping gas was collected in a nitrometer over sodic hydrate solution. The gas burned with the greenish flame of ethyl chloride. The contents of the tube were then rinsed into a flask with a small amount of benzene and cold, dry ligroïn added. A small amount of a colorless oil (A) was precipitated. Its color resembled that of the other urea chlorides. A part of this oil was added to aniline. The reaction with aniline was very violent and a white solid was obtained. The substance was washed with dilute hydrochloric acid and, recrystallized from hot water and from dilute alcohol, it melted sharply at 106°. Analysis showed it to have the composition $C_{10}H_{12}N_2O_3$.

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[1] Loeb: Ber. d. chem. Ges.. **19**, 2344.

[2] Gattermann: *loc. cit.*

I. 0.2563 gram substance gave 31.3 cc. moist nitrogen at 741.7 mm. and 21°.

II. 0.2159 gram substance gave 0.454 gram CO_2 and 0.1162 gram H_2O.

	Calculated for $C_{10}H_{12}N_2O_3$.	Found.
N	13.46	13.62
C	57.69	57.35
H	5.77	5.98

The formula $C_{10}H_{12}N_2O_3$ corresponds to that of phenylallophanic ether, which could have been formed as follows:

$$NH_2COOC_2H_5 + COCl_2 = ClOCNHCOOC_2H_5 + HCl.$$

$$C_2H_5O_2CNHCOCl + NH_2C_6H_5 = C_6H_5NHCONHCOOC_2H_5 + HCl.$$

Stojenten,[1] however, who prepared phenylallophanic ether, by the action of ethoxal chloride on monophenyl urea, gives its melting-point as 120°. Another quantity of the above compound was, therefore, prepared and purified by dissolving in sodic hydrate and precipitating it in the filtrate with hydrochloric acid and then recrystallizing the dry substance from ether and ligroïn. It still melted sharply at 106° and the analyses confirmed the composition $C_{10}H_{12}N_2O_3$.

I. 0.1653 gram substance gave 0.3492 gram CO_2 and 0.0868 gram H_2O.

II. 0.1605 gram substance gave 0.3388 gram CO_2 and 0.0849 gram H_2O.

	Calculated for $C_{10}H_{12}N_2O_3$.	Found.	
		I.	II.
C	57.69	57.61	57.57
H	5.77	5.83	5.87

In view of the discrepancy between the melting-point found by Stojenten and by myself it was decided to prepare phenylallophanic ether synthetically.

Synthesis of Phenylallophanic Ether, $C_6H_5NHCONHCOOC_2H_5$.—It was expected that phenyl isocyanate would readily take up urethane and give phenylallophanic ether,

$$C_6H_5NCO + H_2NCOOC_2H_5 = C_6H_5NHCONHCOOC_2H_5.$$

It was found, however, that phenylisocyanate and urethane react only with great difficulty and in a different manner. Molecular quantities were heated to 55° for one hour, and to 160° for one hour; but in no case could allophanic ether be obtained. A mixture of two substances, one melting at about 173° and the other at about 195°, was formed; but these were not further examined; they are probably cyanuric acid derivatives.

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[1] J. prakt. Chem. [2], 32, 18.

A much smoother reaction results if chlorformanilide, $C_6H_5NHCOCl$, the hydrochloric acid addition-product of phenyl isocyanate, is substituted for the latter. 1.5 grams chlorformanilide (1 mol.) and 0.86 gram urethane (1 mol.) were heated to 100° for half an hour. The contents had still a strong odor of isocyanate, but solidified on cooling. The substance was purified by precipitation from alkaline solution and recrystallized from alcohol. The phenylallophanic ether obtained according to the equation,

$$C_6H_5NHCOCl + H_2NCO_2C_2H_5 = C_6H_5NHCONHCO_2C_2H_5 + HCl,$$

melted sharply at 106°, and when this synthetic product was mixed with the compound $C_{10}H_{12}N_2O_3$ above referred to its melting-point was not changed. This compound is, therefore, phenylallophanic ether, and the low melting-point is undoubtedly the correct one.[1] Stojenten's phenylallophanic ether was separated from phenylparabanic acid (melting-point 208°) by fractional precipitation, and it is possible that he mistook a mixture for pure phenylallophanic ether.

In order to show that the oil (*A*) from which phenylallophanic ether was obtained by means of aniline was not a mixture simply of unchanged urethane and phosgene, which could give phenylallophanic ether according to the equation,

$$C_6H_5NH_2 + COCl_2 + H_2NCOOC_2H_5 = 2HCl + C_6H_5NHCONHCO_2C_2H_5,$$

but contained chlorformylurethane, I dissolved a mixture of aniline and urethane in benzene, and added phosgene. The mixture reacted very violently, and carbanilide (melting-point 235°) was obtained, but not a trace of phenylallophanic ether. This proves that the formation of phenylallophanic ether in the above reaction with aniline is due to the presence of a chloride, $C_2H_5O_2CNHCOCl$, *chlorformylurethane*, which is formed from phosgene and urethane, as follows:

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[1] *Vide* analyses.

$$NH_2COOC_2H_5 + COCl_2 = C_2H_5O_2CNHCOCl + HCl.$$

The presence of chlorformylurethane in the oil *A* was confirmed by converting it by means of ammonia into allophanic ether. The oil *A*, as shown below, contains a very small quantity of allophanic ether, from 10 grams phosgene and 8 grams urethane, half a gram of allophanic ether being obtained. If the oil *A* be divided into two equal portions and dry ammonia be passed into one portion dissolved in benzene, this will give about 6 grams allophanic ether (melting-point 192°), while the other portion, treated in exactly the same way, but without passing ammonia into it, gives only about half a gram of allophanic ether. The allophanic ether is formed as follows:

$$C_2H_5O_2CNHCOCl + NH_3 = C_2H_5O_2CNHCONH_2 + HCl,$$

confirming the presence of chlorformylurethane in the oil *A*.

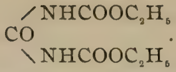
Besides this substance, the oil *A* contains at least two others. A part of this oil obtained from the first action of phosgene on urethane was left in a desiccator. On standing, this soon became somewhat turbid, and a white solid gradually formed until it consisted of a semi-solid mixture. Water was carefully added, and the mixture extracted with cold ether. From this ether-extract was obtained a small amount of a white crystalline compound which was recrystallized from ether and ligroïn and melted at 107°.

I. 0.1582 gram substance gave 18.8 cc. moist nitrogen at 755.2 mm. and 16.5°.

II. 0.1900 gram gave 0.2902 gram CO_2 and 0.1046 gram H_2O.

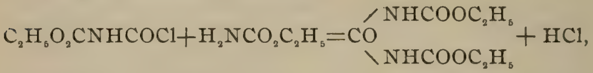
	Calculated for $C_7H_{12}N_2O_5$.	Found. I.	II.
N	13.73	13.78	....
C	41.18	....	41.66
H	5.88	....	6.10

The analysis show this substance to have the composition $C_7H_{12}N_2O_5$, corresponding to carbonyldiurethane,



$$\mathrm{CO}\begin{matrix}\diagup \mathrm{NHCOOC_2H_5}\\ \diagdown \mathrm{NHCOOC_2H_5}\end{matrix}.$$

It is formed by the action of the chloride $C_2H_5O_2CNHCOCl$, on a second molecule of urethane,



$$\mathrm{C_2H_5O_2CNHCOCl + H_2NCO_2C_2H_5 = CO}\begin{matrix}\diagup \mathrm{NHCOOC_2H_5}\\ \diagdown \mathrm{NHCOOC_2H_5}\end{matrix} + \mathrm{HCl},$$

and is the carbonyldiurethane, which Loeb thought might be formed in his reaction, as an unstable intermediate product, and, on being recrystallized, give allophanic ether with loss of carbon dioxide and alcohol, but which had never been obtained before this.

Carbonyldiurethane is, as a matter of fact, a very stable substance. It suffers no decomposition on being recrystallized from any organic solvent or from water. It was heated in a sealed tube with a benzene solution of hydrochloric acid to 75°–80° for half an hour without change. Carbonyldiurethane cannot, therefore, be considered as an intermediate product in the formation of allophanic ether, as supposed by Loeb, but is one of the final products of the action of undiluted phosgene on urethane.

In the oil *A* there is a small quantity of a third substance, as already mentioned, *viz.*, allophanic ether. It remained after the carbonyldiurethane had been extracted with ether, and was recrystallized from alcohol, and identified by its melting-point (192°) which remained unchanged, when the substance was mixed with synthetic allophanic ether. Since carbonyldiurethane is perfectly stable and is not converted into allophanic ether under the conditions described, the formation of allophanic ether is best explained as follows: Besides acting on the amide group of urethane, phosgene, in a secondary reaction, splits off alcohol from urethane, the cyanic acid formed uniting at once with the liberated hydrogen chloride, giving chlorformamide. This in turn yields with a second molecule of urethane allophanic ether,[1]

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[1] Gattermann: *Loc. cit.*

$NH_2COOC_2H_5 + COCl_2 = NH{=}CO + CO_2 + HCl + ClC_2H_5$,
$NH_2COCl + H_2NCOOC_2H_5 = NH_2CONHCO_2C_2H_5 + HCl$.

This view is strongly supported by the fact that allophanic ether is obtained from urethane, indifferently by using a number of similar chlorides as thionyl chloride,[1] phosphorus oxychloride,[2] and, as a by-product, even in the action of benzoyl chloride on urethane,[3] where the main product is also benzoylurethane, $C_6H_5CONHCO_2C_2H_5$, as with phosgene. The above explanation satisfies all of these cases.

The action of phosgene on urethane is, therefore, threefold, as may be briefly summarized by the following equations :

To a limited extent we have

(1) $NH_2COOC_2H_5 + COCl_2 = NH_2COCl + ClC_2H_5 + CO_2$,
$NH_2COCl + NH_2COOC_2H_6 = NH_2CONHCOOC_2H_5 + HCl$.

To a far greater extent we have

(2) $COCl_2 + NH_2COOC_2H_5 = ClCONHCOOC_2H_5 + HCl$.

This chloride, being also quite reactive, acts on a second molecule of urethane, so that we have also

(3) $C_2H_5OOCNHCOCl + NH_2COOC_2H_4 = CO(NHCO_2H_5)_2 + HCl$.

Carbonyldiurethane, $CO(NHCOOC_2H_5)_2$.—If in accordance with the last two equations two molecules of urethane be taken to one of phosgene, and the mixture heated to 85° for half an hour, the yield of diurethane is very largely increased. The best yield was obtained as follows : To two molecules of urethane and from one to two molecules of pyridine[4] was added one molecule of phosgene, contained in a loosely-stoppered tube so as to prevent any action taking place, before sealing the larger tube. The mixture was heated to 85° for thirty minutes, and the contents washed out with a small quantity of water. The water dissolved the pyridine and the pyridine hydrochloride, precipitating nearly all the carbonyldiurethane in a very pure condition. About eight grams diurethane was obtained from ten grams phosgene by this method. Carbonyldiurethane consists of white plates, and is very soluble in all the organic solvents except ligroïn. It is also readily soluble in hot water and in alkalies.

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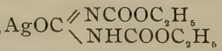
[1] Schroeter and Levinsk : Ber. d. chem. Ges., **26**, 2171. [2] *Vide* p. 343, (this paper).
[3] Pechmann and Vanino : Ber. d. chem. Ges., **28**, 2383.
[4] *Vide* Pechmann and Vanino : *loc. cit.*

Silver Carbonyldiurethane,



$AgOC\begin{cases} /\!/NCOOC_2H_5 \\ \backslash NHCOOC_2H_5 \end{cases}$. —From the solution of carbonyldiurethane in alkalies a silver salt can be prepared by precipitating with silver nitrate. The silver salt contains only one atom of silver to each molecule of carbonyldiurethane; my attempts to make it take up two atoms of silver were all unsuccessful. If the compound be dissolved in dilute caustic potash solution containing two molecules potassic hydrate, or a little more than one molecule, the white precipitate which is produced by each drop of silver nitrate solution is at once mixed with the brown oxide of silver. With the ammonia solution of carbonyldiurethane silver nitrate gives no precipitate.

The best method for preparing the pure silver salt I found to be the following: Diurethane was dissolving in dilute caustic potash solution containing a trifle less than one molecule potassic hydrate. Silver nitrate solution in excess was then added with constant stirring. A bulky, gelatinous precipitate, which is very difficult to wash, is thus formed. The mixture was, therefore, left standing in a dark place for twelve hours; the precipitate remained perfectly white. It was then filtered, and washed with cold water and dried in a desiccator. The dry salt was powdered and again washed very thoroughly with cold water, being kept in the dark as much as possible. By this method I obtained the salt pure, and very little colored. A small amount of alkali is liable to cling to it with the greatest tenacity, and cannot be removed from the freshly prepared, gelatinous salt, either by cold or by hot water. The salt is, besides, somewhat soluble in hot water, and to some extent decomposed by it. 4.9 grams of this pure salt was obtained from 4 grams carbonyldiurethane.

I. 0.2488 gram substance gave 0.2441 gram CO_2 and 0.0858 gram H_2O.

II. 0.3191 gram substance gave 26.4 cc. moist nitrogen at 740.2 mm. and 27.5°.

III. 0.3918 gram substance gave 0.13673 gram Ag.

	Calculated[1] for $C_7H_{11}N_2O_5Ag$.	Fouud.
C	27.04	26.76
H	3.54	3.83
N	9.01	8.92
Ag	34.66	34.90

The results obtained in the experiments described in this paper may be summarized as follows·

(1) The reaction

$$RCONHBr + NaOCH_3 = RNHCOOCH_3 + NaBr,$$

is quite as general as the analogous reaction of alkalies on acid bromamides, and should be quite as useful in the preparation of urethanes as is the reaction of Hofmann in the preparation of amines. The introduction of negative groups into the radical R does not prevent the "Beckmann rearrangement" of the acid bromamides by sodium methylate with the formation of urethanes, and in no case was direct substitution of the bromine atom effected even to a slight extent. This result is in entire accord with the results of Hoogewerff and Van Dorp with aqueous alkalies. The introduction of positive groups, as far as determined by the single case where such a bromamide was examined, has no more influence than that of negative groups.[2]

(2) The reaction of phosphorus pentachloride on urethanes according to the equation

$$RNHCOOCH_3 + PCl_5 = RNHCOCl + CH_3Cl + POCl_3$$

is also general in the urethanes of the aromatic amines.

The above two reactions together give easy methods for preparing chlorformanilides and isocyanates. The chlorformanilides thus prepared are often much more reactive than the corresponding isocyanates, as shown in the synthesis of phenylallophanic ether, and can be used with advantage in their place.

(3) With free urethane, $NH_2COOC_2H_5$, phosphorus pentachloride splits off ethyl chloride and a carbamide chloride is

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[1] NOTE.—Mr. F. B. Dains, working under the direction of Dr. Stieglitz, is studying the constitution of this silver salt, and has already obtained an alkyl derivative corresponding to the constitution indicated.

[2] The investigation on the effect of positive groups is being continued in this laboratory.

formed; but the reaction is not so simple as with the aromatic urethanes; the phosphoric chloride most likely enters the amide group, giving phosphoric acid derivatives of chlorformamide.

(4) Phosgene and urethane when brought together in molecular proportions react simultaneously in three different ways:

1. $NH_2COOC_2H_5 + COCl_2 = ClCONHCOOC_2H_5 + HCl.$
2. $ClCONHCOOC_2H_5 + H_2NCOOC_2H_5 = CO(NHCOOC_2H_5)_2 + HCl.$
3. $2NH_2COOC_2H_5 + COCl_2 = NH_2CONHCOOC_2H_5 + ClC_2H_5 + CO_2 + HCl.$

The first two reactions can be regulated to a large extent by adding an excess of one or the other of the reacting substances. The third reaction, on the other hand, occurred to a small extent in all the reactions of phosgene on urethane as it apparently does in the action of any acid chloride on urethane.

The above investigations were pursued under the direction of Dr. Stieglitz, and I wish here to express my sincere appreciation of the thoughtfulness with which he guided and assisted me in the work.

ACTION OF PHOSPHORUS PENTACHLORIDE ON ANILINE AND ITS SALTS.

BY J. ELLIOTT GILPIN.

The constant occurrence of chlorphosphuret of nitrogen $(PNCl_2)_3$ as a by-product in the formation of orthosulphobenzoic acid from commercial saccharine directed attention in this laboratory to this very interesting substance. Discovered by Liebig, it was studied by Liebig and Wöhler,[1] Gladstone and Holmes,[2] Laurent,[3] Wichelhaus,[4] Hofmann,[5] and Stokes.[6] Hofmann studied its action with aniline and paratoluidine, and obtained derivatives in which the chlorine had been replaced by residues of aniline and paratoluidine, the product with the aniline having the composition $P_3N_3(NHC_6H_5)_6$. Besson[1] has repeated the work done on this substance and obtained the compound $PNCl_2$. He says the compound described by Gladstone as having the composition $(PNCl_2)_3$ and the melting-point 210° is probably a polymeric form of $PNCl_2$; but there is evidently some mistake here, as Gladstone found the melting-point to be 110° and not 210°, while according to Besson it is 114°. As the formation of the chlorphosphuret of nitrogen is due to the action of phosphorus pentachloride on ammonium chloride, the possibility was suggested of obtaining a derivative of it by using instead of ammonium chloride a substitution-product, aniline hydrochloride. Although the substance obtained in this action is not a derivative of the chlorphosphuret of nitrogen, still a comparison of the two forms an interesting study. They show the tendency of phosphorus and nitrogen to combine sometimes in a very stable form as in the chlorphosphuret of nitrogen and a substance obtained in this investigation, which will be discussed later. The former can be heated with concentrated acids and alkalies without undergoing change; but the trichlorphosphanil, obtained in this work, is very unstable, decomposing with nearly all reagents, and even slowly when exposed to moisture.

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[1] Ann. Chem. (Liebig), **11**, 139.

[2] Ann. Chem. (Liebig), **76**, 74.

[3] Compt. Rend., 1850, Sep. (9).

[4] Ber. d. chem. Ges., **3**, 163.

[5] Ber. d. chem. Ges., **16**, 1910.

[6] This JOURNAL, **17**, 275.

Up to the time when this investigation was begun the study of the action of aniline on the chlorides of phosphorus had not led to satisfactory results, and the action with the trichloride only had been studied. By the action of aniline on phosphorus trichloride, Tait[2] obtained a compound to which he gave the formula $P(NH_2C_6H_5Cl)_3$. Jackson and Menke[3] repeated this work, but were unable to obtain the product described by Tait. They obtained a product which they thought had the composition $PCl(NHC_6H_5)_2$, but were unable to isolate it. By dissolving it in alcohol and precipitating with water they obtained the compound $P(OH)(NHC_6H_5)_2$, which they considered to be its hydroxyl derivative. Weyer[4] studied the action of aniline on trichloride of arsenic, and obtained two definite products by the successive substitution of aniline residues for the chlorine atoms. These were represented by the formulas $AsCl_2(NHC_6H_5)$ and $AsCl(NHC_6H_5)_2$. The third step he was unable to take. In the present investigation, in which the action of phosphorus pentachloride on aniline and its salts is under investigation, four definite substances have been isolated. They are formed by the substitution of residues of aniline for one or more chlorine atoms of the phosphorus pentachloride, one being obtained by the action of phosphorus pentachloride on aniline hydrochloride, and three by the action on aniline. The trichlorphosphanil, having the composition $PCl_3(NC_6H_5)$, which was obtained from the aniline hydrochloride, shows great similarity to the first derivative obtained by Weyer. They are both very sensitive to moisture, and decompose with water and alcohol in a similar manner. The other substances were more stable, and were obtained from their solutions in alcohol in the form of well-defined crystals.

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[1] Compt. Rend., **114**, 1264.

[2] Ztschr. Chem., 1865, 648.

[3] This JOURNAL, **6**, 89.

[4] Dissertation, Bonn, 1891.

During the progress of this investigation an article by Michaelis and Schroeter[1] has appeared, in which a substance, formed by the action of aniline on phosphorus trichloride, of the composition $C_6H_5N—PCl$, is described. This substance bears the same relation to phosphorus trichloride, as the trichlorphosphanil, described in this paper, does to phosphorus pentachloride.

Action of Phosphorus Pentachloride on Aniline Hydrochloride— Trichlorphosphanil $PCl_3(NC_6H_5)$.

After considerable experimenting, the following method was adopted as the best for the preparation of this substance: Phosphorus pentachloride and perfectly dry aniline hydrochloride are mixed in molecular quantities, not more than ten grams of the aniline hydrochloride being used at a time. The intimately mixed compounds are placed in a distilling-bulb, and connected with a condenser. A tube at the lower end of the condenser passes into a vessel of water, to absorb the hydrochloric acid formed, and show the rate of the action. The bulb is half immersed in a sulphuric-acid bath. Before the temperature at which the trichlorphosphanil is formed is reached, a small quantity of phosphorus pentachloride sublimes in the upper part of the neck. If the temperature is kept at 170° for six to eight hours, the trichlorphosphanil condenses on the cool part of the bulb, and sometimes in the condenser, as a white coating, covered on the inside with nodules. After the evolution of hydrochloric acid has ceased, the material can be obtained in a very pure condition, if the part in the neck of the bulb is discarded. After being powdered, it is placed in a desiccator over caustic potash to remove the hydrochloric acid. It must be kept perfectly dry, and cannot be purified by crystallization, as water, alcohol, ether, acetone, and other solvents decompose it. Even when resublimed some decomposition takes place. In every case there was a small quantity of a dark, green, sticky material left in the bulb after the action was over. This may have been due to impurities in the phosphorus pentachloride, as the ordinary commercial article was used. When heated with water this green material acts quite violently at first, in consequence no doubt of the presence of a small excess of phosphorus pentachloride, and a tar-like mass is formed, which is unacted on by water, alkali, and dilute acid, and solidifies on cooling. It is soluble in alcohol, with a green color; so some was dissolved in alcohol and precipitated by addition of water, filtered and washed. This was repeated several times, and the green powder obtained was analyzed ; but different preparations varied in composition, and it was evidently not a single definite compound.

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[1] Ber. d. chem. Ges., **27**, 490.

The formation of the trichlorphosphanil probably takes place as represented in the following equation :

$$PCl_5 + C_6H_5NH_2HCl = PCl_3(NC_6H_5) + 3HCl.$$

Concentrated sulphuric and nitric acids both decompose it, the former with the evolution of hydrochloric acid. Alcohol and ether act on it with the evolution of hydrochloric acid and the generation of considerable heat. Sodium hydroxide acts on it to a slight extent, and changes it to a hard, brittle mass. When boiled with water it is decomposed into aniline, hydrochloric and phosphoric acids, so that the chlorine and phosphorus can be determined in the same specimen, the chlorine as silver chloride, and the phosphorus as magnesium pyrophosphate. To be sure that none of the hydrochloric acid was lost in boiling, several determinations were made by the Carius method, but they agreed with those made in the other way.

The following are the results of the analyses:

Preparation I.

0.3662 gram of the substance gave 0.6754 gram AgCl.
0.2848 gram of the substance gave 0.5226 gram AgCl.
0.2560 gram of the substance gave 0.4672 gram AgCl.
0.3662 gram of the substance gave 0.1788 gram $Mg_2P_2O_7$.
0.2848 gram of the substance gave 0.1367 gram $Mg_2P_2O_7$.
0.2560 gram of the substance gave 0.1242 gram $Mg_2P_2O_7$.
0.2755 gram of the substance gave 0.0609 gram H_2O and 0.3196 gram CO_2.
0.4078 gram of the substance gave 22 cc. N at 16° and 772.5 mm.

Preparation II.

0.2568 gram of the substance gave 0.4635 gram AgCl.
0.3535 gram of the substance gave 0.6354 gram AgCl.
0.3535 gram of the substance gave 0.1695 gram $Mg_2P_2O_7$.
0.4237 gram of the substance gave 23 cc. N at 11°.5 and 762 mm.
0.3698 gram of the substance gave 0.0765 gram H_2O and 0.4081 gram CO_2.
0.3646 gram of the substance gave 0.0748 gram H_2O and 0.4078 gram CO_2.

	Calculated for $PCl_3(NC_6H_6)$.	Found.					
		Preparation I.			Preparation II.		
C	31.55	....	31.63	....	30.09	....	30.50
H	2.19	....	2.45	....	2.29	....	2.27
Cl	46.53	45.59	45.36	45.11	44.43	....	44.61
P	13.58	13.64	13.41	13.56	....	13.40	....
N	6.17	....	6.38	....	....	6.47	....

While these results leave much to be desired, they point clearly to the formula given, and are fairly satisfactory, considering the instability of the substance.

The sulphate and nitrate of aniline were also treated with phosphorus pentachloride, but they did not act like the hydrochloride. The action of the nitrate was very violent, taking place as soon as they were mixed, without the aid of heat. The whole mass was carbonized in a short time. Paratoluidine hydrochloride was also treated with phosphorus pentachloride, but no volatile product was formed.

Decomposition of Trichlorphosphanil with Water.

When trichlorphosphanil is heated with water it first melts and forms an oil which is decomposed by further boiling. The decomposition gives rise to the formation of aniline, and hydrochloric and phosphoric acids, and can be represented thus:

$$PCl_3(NC_6H_5) + 4H_2O = C_6H_5NH_2.HCl + 2HCl + H_3PO_4.$$

The crystals which separated out, after decomposing with water and evaporating, were recrystallized and analyzed. The results of the analyses showed it to be aniline hydrochloride. Another portion was decomposed with water, an excess of barium hydroxide added to liberate the aniline, and this then distilled off. After filtering off the excess of the hydroxide, the presence of barium chloride was proved, showing that free hydrochloric acid had been present. The barium was precipitated with sulphuric acid and the phosphoric acid obtained by evaporating the solution.

Decomposition of Trichlorphosphanil with Sulphuric Acid.

Trichlorphosphanil dissolves in warm concentrated sulphuric acid, with evolution of hydrochloric acid gas. An equal volume of water is added to this, and the liquid is allowed to stand, when a substance crystallized out which was found to be sulphanilic acid. Several of its salts were made and analyzed.

Action of Phosphorus Pentachloride on Aniline. Chlorphostetranilide, $PCl(NHC_6H_5)_4$.

When phosphorus pentachloride is slowly added to aniline and the mass constantly stirred, there is immediate action and hydrochloric acid is evolved. The whole mass becomes hot, and after all the aniline has been used up, and further addition of phosphorus pentachloride causes no action, it solidifies. This mass, when cool, is broken up and heated with water to extract any aniline hydrochloride and phosphorus pentachloride present, then filtered, washed, and dried. This product, which is a light-yellow powder, is insoluble in water, but slightly soluble in alcohol. It consists largely of one substance, but several others are present in small quantities.

If the dried mass is shaken with two separate quantities of cold alcohol, and the liquid, after being filtered, is allowed to evaporate slowly, besides some needle-shaped crystals there will be found some well defined monoclinic crystals, which grow to a considerable size. These have to be separated from the other product mechanically. If the solution from which these have been obtained is filtered and allowed to evaporate still further, in some cases, tufts of fine, radiating, silky needles separate out. Both these and the large crystals will be discussed later. After treating several times with cold alcohol, the original material is treated repeatedly with small quantities of hot alcohol, until on evaporation only one substance separates out from the solution. By this process a definite substance is obtained in pure condition. This is slightly soluble in alcohol and insoluble in water. When crystallized from alcohol it usually consists of long, irregular-shaped crystals; but, when the evaporation is very slow, and absolute alcohol is used, monoclinic crystals with well defined basal planes and fundamental prisms, are formed. The composition of this substance is represented by the formula $PCl(NHC_6H_5)_4$, and its mode of formation is expressed as follows:

$$PCl_5 + 4C_6H_5NH_2 = PCl(NHC_6H_5)_4 + 4HCl.$$

It is not decomposed when boiled with water, concentrated alkali, or hydrochloric acid; but when heated with water in a sealed tube to 180° for several hours, aniline, aniline hydrochloride, and phosphoric acid are formed. This substance is characterized by its great insolubility. It is practically insoluble in ethyl ether, acetone, benzene, ligroïn, and amyl alcohol; but slightly soluble in ethyl alcohol. When heated, a volatile product, which proved to be a mixture of aniline, aniline hydrochloride, and some diphenylamine hydrochloride, formed by the action of aniline on aniline hydrochloride, was formed, and an amorphous black substance remained. The great stability of this substance is shown by the fact that *only a small amount was decomposed when it was heated in a porcelain tube, in a current of oxygen, over the blast-lamp for several hours.*

A qualitative analysis of this substance showed that it contains phosphorus, nitrogen, and carbon. The black stable residue is very similar to a product described by Rose.[1] By the action of phosphorus trichloride on ammonia he obtained a product to which he gave the formula $PCl_3 + 5NH_3$. When this was heated, ammonium phosphate and ammonium chloride were formed, and a white substance, phospham, PN_2H, was left behind. A comparison of this and the black residue is worthy of notice. Neither is soluble in water or dilute acids. They are only partly decomposed by boiling with fuming nitric acid for some time. Concentrated sulphuric acid attacks the phospham; but acid potassium sulphate is necessary to decompose the black residue. Neither is acted on when heated in a stream of chlorine. They are decomposed by fused alkali, and also with generation of phosphorus or a compound of phosphorus and hydrogen, when heated to redness in a current of hydrogen. The black residue may also contain a small amount of hydrogen; but this cannot be considered as certain, for the decomposition of the substance is accomplished with so great difficulty that the sources of error introduced may account for the presence of the hydrogen.

The formation of this compound prevented the determination of the carbon and hydrogen by the usual method in the case of all the compounds studied, except that of the trichlorphosphanil, which is volatile. In some cases, when the substances were heated in platinum boats, a transparent film was formed about the small particles of carbon, preventing their complete combustion. The method finally adopted for the determination of carbon, and the only one by which satisfactory results could be obtained, was that described by Fritsch,[1] in which the substance was oxidized by potassium chromate and sulphuric acid.

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[1] Ann. der. phys. Pogg., 28, 529; Ann. Chem. (Liebig), 11, 130.

The nitrogen was determined both by the absolute and by the Kjeldahl methods. The chlorine and phosphorus were determined as silver chloride and magnesium pyrophosphate respectively, the substance being decomposed by heating it with fuming nitric acid in a sealed tube to 180° for several hours.

Analysis of the Dry Powder.

Preparation I.

The specimen of aniline used for this was not purified and was very dark, and the products retained some of the impurities.

0.2332 gram of the substance gave 0.0746 gram AgCl.
0.19765 gram of the substance gave 0.0631 gram AgCl.
0.2102 gram of the substance gave 0.0553 gram $Mg_2P_2O_7$.
0.154 gram of the substance gave 0.3724 gram CO_2.
0.1974 gram of the substance gave 0.4784 gram CO_2.

Preparation II.

0.2366 gram of the substance gave 0.0784 gram AgCl.
0.2366 gram of the substance gave 0.0595 gram $Mg_2P_2O_7$.
0.2096 gram of the substance gave 0.0691 gram AgCl.
0.2096 gram of the substance gave 0.0552 gram $Mg_2P_2O_7$.
0.488 gram of the substance 0.0633144 gram N (Kjeldahl).
0.189 gram of the substance gave 22.23 cc. N. at 25.8° and 758.8 mm.
0.1584 gram of the substance gave 0.3863 gram CO_2.

Preparation III.

0.1966 gram of the substance gave 0.0655 gram AgCl.
0.2025 gram of the substance gave 0.494 gram CO_2.

Analyses of the Crystals.

0.2258 gram of the substance gave 0.057 gram $Mg_2P_2O_7$.
0.2309 gram of the substance gave 0.0792 gram AgCl.
0.2309 gram of the substance gave 0.0612 gram $Mg_2P_2O_7$.

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[1] Ann. Chem. (Liebig), **294**, 79.

0.2324 gram of the substance gave 0.0792 gram AgCl.
0.1613 gram of the substance gave 0.0553 gram AgCl.
0.1613 gram of the substance gave 0.0435 gram $Mg_2P_2O_7$.
0.1483 gram of the substance gave 0.0503 gram AgCl.

	Calculated for $PCl(NHC_6H_5)_4$.	Found (powder). Preparation I.			II.		III.
Cl	8.14	7.90	7.89	...	8.19	8.14	8.24
P	7.13	...	...	7.44	7.02	7.36	...
N	12.89	...	...	...	12.97	13.04	...

		Found (crystals).				
Cl	8.14	....	8.47	8.42	8.47	8.38
P	7.13	7.05	7.40	...	7.53	...
N	12.89	....	...	...	...	...
C	66.29	65.94	66.09	...	66.50	66.52

Attempts made to substitute a residue of aniline for the chlorine atom in the compound, $PCl(NHC_6H_5)_4$, have up to the present been unsuccessful. Some of the powder was added to boiling aniline, in which it readily dissolved; but the product which separated out when it cooled had the same composition as the original material.

Action of Sulphuric Acid on Chlorphostetranilide, $PCl(NHC_6H_5)_4$.

When chlorphostetranilide is treated with concentrated sulphuric acid, hydrochloric acid is given off, and the substance goes into solution. If the acid is warmed and saturated with the tetranilide it becomes solid, with crystals, on cooling. The following method was used for the preparation of the compound formed in the action:

The tetranilide was treated with as small a quantity of sulphuric acid as possible, and the solution warmed to complete the decomposition and expel the hydrochloric acid. After cooling, water was added, in volume about twice that of the acid, and the solution heated to dissolve the substance precipitated by the water. This solution, on standing, deposits clear, octahedral crystals, which can be filtered off, and recrystallized from water. These crystals are extremely efflorescent, and begin to lose their water of crystallization before the water which they hold mechanically can be removed.

It has acid properties and is very soluble in water and alcohol, as are also the barium and lead salts, which are formed by neutralizing a solution of the acid with barium and lead carbonates, and filtering and evaporating the solutions.

On account of the ease with which these salts dissolve in water, they could not be obtained in a crystallized condition suitable for analysis, but in each case were evaporated to dryness over the water-bath. The action of the sulphuric acid on the tetranilide is as follows:

$$\mathrm{PCl(NHC_6H_5)_4 + 4H_2SO_4 = P(OH)(NHC_6H_4SO_3H)_4 + 3H_2O + HCl.}$$

The sulphur and phosphorus were determined as barium sulphate and magnesium pyrophosphate, respectively. The substance was decomposed according to the Pierson method with nitric acid and potassium chlorate.

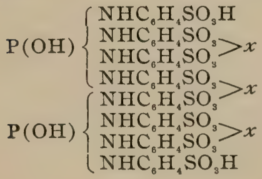
0.1518 gram of the substance gave 0.1927 gram $BaSO_4$.
0.2086 gram of the substance gave 0.0313 gram $Mg_2P_2O_7$.

	Calculated for $P(OH)(NHC_6H_4SO_3H)_4$.	Found.
S	17.39	17.44
P	4.21	4.19

The determinations of the barium and lead in the salts gave the following results:

0.4358 gram of the substance gave 0.1614 gram $BaSO_4$.
0.4499 gram of the substance gave 0.1694 gram $BaSO_4$.
0.6464 gram of the substance gave 0.2741 gram $PbSO_4$.
0.6333 gram of the substance gave 0.2676 gram $PbSO_4$.

These results cannot be explained on the assumption of the formation of a simple compound; but they agree with a salt of the following composition, in which part of the hydrogen of two molecules of the sulphonic acid is replaced by the metals:



$$\begin{array}{ll}\mathrm{P(OH)}\left\{\begin{array}{l}\mathrm{NHC_6H_4SO_3H}\\ \mathrm{NHC_6H_4SO_3}\\ \mathrm{NHC_6H_4SO_3}\\ \mathrm{NHC_6H_4SO_3}\end{array}\right. & \begin{array}{l}\\ \\ >x\\ \\ \end{array}\\ & >x\\ \mathrm{P(OH)}\left\{\begin{array}{l}\mathrm{NHC_6H_4SO_3}\\ \mathrm{NHC_6H_4SO_3}\\ \mathrm{NHC_6H_4SO_3}\\ \mathrm{NHC_6H_4SO_3H}\end{array}\right. & \begin{array}{l}\\ \\ >x\\ \\ \end{array}\end{array}$$

where x = barium or lead.

	Calculated for these salts.	Found. 1.	2.
Ba	21.89	21.78	22.14
Pb	29.69	28.95	28.88

Action of Phosphorus Pentachloride on the Toluidines.

When the three toluidines are treated under the same conditions as the aniline, with phosphorus pentachloride, they give compounds analogous to chlòrphostetranilide. The method of purification was the same as that used with the aniline compound. The results of the analyses were as follows:

Orthotoluidine.

0.2011 gram of the substance gave 0.0599 gram AgCl.
0.2888 gram of the substance gave 0.0692 gram $Mg_2P_2O_7$.

Metatoluidine.

0.213 gram of the substance gave 0.066 gram AgCl.

Paratoluidine.

0.2918 gram of the substance gave 0.0814 gram AgCl.

	Calculated.	Found. Ortho.	Meta.	Para.
Cl	7.21	7.36	7.65	6.89
P	6.32	6.69	...	...

Besides the compounds already mentioned, two other substances have been obtained by treating aniline with phosphorus pentachloride, under different conditions. The results of the investigation carried out on these substances, will be published shortly.

Chemical Laboratory, Johns Hopkins University,
March, 1897.

Contribution from the Sheffield Laboratory of Yale University.

L.—ON THE PREPARATION OF METABROMBENZOIC ACID AND OF METABROMNITROBENZENE.

By H. L. Wheeler and B. W. McFarland.

It is now over thirty years since Reinecke[1] showed that benzoic acid could be directly brominated. His method was to heat the acid with bromine and water, in a closed tube, to

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[1] Ztschr. Chem., 1865, 116; 1869, 109.

100° for several days. Reinecke's method, with the modifications of Hübner, Ohly, Philipp[1], Petermann,[2] and Angerstein[3] for its purification, is given in the last edition of Beilstein's *Handbuch* as the method of preparation ("Darstellung").

Again, according to the above authority, metabromnitrobenzene is best prepared as follows: (*i. e.*, "Darstellung"): "Man erhitzt in Röhren von 150 cc. Inhalt je 25 g. Nitrobenzol mit 32.5 g. (über H_2SO_4 entwässertem) Brom und 1 g. pulverisirten Eisenchlorid zwölf Stunden lang auf 60°–70°." This is Scheufelen's[4] method and it gives a yield of over 80 per cent. of the calculated quantity of pure metabromnitrobenzene.

Scheufelen also showed that ferrous bromide would readily effect the bromination in closed tubes. An experiment of his in an open vessel was not a success, however, since only 25 per cent. of the theoretical yield of metabromnitrobenzene was obtained.

The above methods can be greatly simplified, inasmuch as the operations can be performed in a short time and without the use of closed tubes if iron be used as a bromine carrier. Moreover, contrary to the result of Scheufelen, a yield of metabromnitrobenzene almost equal to that obtained in closed tubes with ferrous bromide, can be obtained in open vessels by the use of iron.

Iron, as a bromine-carrier, is now frequently used in other cases, since it often effects bromination with surprising readiness. This property of iron is well illustrated with paradichlorbenzene. (See below.) From the experiments with iron and ferrous bromide, in the case of nitrobenzene, it appears that iron is a better carrier of bromine than separately prepared ferrous bromide and naturally more convenient.

Metabrombenzoic Acid.—After a number of experiments we have come to the conclusion that the following is the best method for the preparation of this acid: 20 grams of benzoic acid and 6 grams of iron wire or gauze are placed together in a flask connected with a condenser and heated on a metal bath. When the temperature of the bath reaches about 170° 48 grams of bromine are added, drop by drop, while the temperature of the bath is allowed to rise until at the end of the operation it reaches 260°. The addition of the bromine requires about one hour and a half, with the above quantities, when the bromination is finished. The quantity of bromine given is sufficient to convert all the iron into ferrous bromide, the benzoic acid into monobrombenzoic acid, and then allow 4.7 grams for loss. Generally, however, not all the iron is attacked and some dibrombenzoic acid results.

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[1] Ann. Chem. (Liebig), **143**, 233.

[2] *Ibid.*, **149**, 131.

[3] *Ibid.*, **158**, 5.

[4] *Ibid.*, **231**, 165.

After the bromine has been added the mass is dissolved in sodium hydroxide, filtered from the iron and ferric hydroxide, and after precipitating the metabrombenzoic acid with hydrochloric acid it can then be purified in the usual way. We proceeded as follows in the purification: After precipitating the acid with hydrochloric acid it was shaken out with ether. This gave a crude product weighing 32 grams; calculated weight for monobrombenzoic acid, 32.9 grams. This was distilled and the portion boiling below 300° (none came over below 280°), and weighing 20 grams, was crystallized once from 50-per cent. alcohol. It melted from 145°–148° and was therefore practically pure metabrombenzoic acid. From this it will be seen that the yield of the acid does not lie far short of being equal to the weight of benzoic acid employed. The same material crystallized three times from benzene melted at 152°–153°, which is the melting-point usually assigned to the pure acid.[1]

Perbrombenzene, C_6Br_6.—An experiment in a closed tube gave perbrombenzene as the sole product. The carboxyl group of the acid being displaced, 5 grams of benzoic acid, 2 grams of iron, and 37.4 grams of bromine were heated in a tube to 225° for five hours. On opening the tube great pressure was observed and the bromine had entirely disappeared.

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[1] Metabrombenzoic acid resembles benzoic acid in the manner in which its melting-point is lowered by a slight amount of impurity or admixture. Friedburg (Ann. Chem. (Liebig), **158**, 23) states that the pure acid melts at 155°, and that benzoic acid melts at 121°, while a mixture of these acids containing 20 per cent. of benzoic acid melts as low as 115°, and therefore 6° lower than benzoic acid. With larger amounts of impurities the melting-point of the mixture was observed as low as 96°, and, as Friedburg states: "Man sieht also, das man sich nicht wundern darf, bei der Bereitung der Brombenzoesäure niedrig schmelzende Gemische zu erhalten."

The crystalline product obtained was difficultly soluble in the ordinary solvents; from benzene it separated in the form of needles and did not melt below the boiling-point of sulphuric acid.

Metabromnitrobenzene.—30 grams of nitrobenzene and 3 grams of iron wire are placed in a flask with reversed condenser and heated up to 120° in an oil-bath. 60 grams of bromine are then gradually added, the operation taking about three-quarters of an hour. The flask is left in the bath for three-quarters of an hour more, and then the contents distilled in steam. The crude, almost pure, product thus obtained after pressing on paper and drying amounts generally to about 75 per cent. of the calculated. We have obtained a yield, however, as high as 85 per cent. by the above method. In one experiment using three times the above quantities a yield of 64 per cent. of the calculated was obtained. These results, although somewhat lower than the best obtained in closed tubes, are highly satisfactory when one considers the greater time required and the other disadvantage in the closed-tube method.

1,4-Dichor-2,5-dibrombenzene (?).–An experiment with paradichlorbenzene was interesting as a further illustration of the ease with which iron often effects bromination. Paradichlorbenzene, when pure, can be boiled with its own volume of bromine and the bromine all driven off without altering its melting-point or without its giving off hydrogen bromide. If, however, a piece of iron be added to the warmed mixture, a strong effervescence takes place, hydrogen bromide is given off, and the reaction proceeds of itself, the product soon solidifying. After pulverizing and washing out the iron bromide, the residue can be crystallized from hot absolute alcohol, in which it is difficultly soluble. It then gives beautiful colorless needles or prisms which melt at about 148°. A product thus obtained gave the following results on analysis:

	Found.	Calculated for $C_6H_2Cl_2Br_2$.
Cl	23.26	23.31
Br	52.33	52.46

This is presumably 1,4-dichlor–2,5-dibrombenzene, the corresponding tetrabrombenzene which it resembles in regard to solubility, etc., being also formed by direct bromination. With the exception of the fact that it was found that this compound is very unreactive, it was not further investigated, test-tube experiments showing that it was not affected appreciably by boiling with nitric acid, and that it could be volatilized from fused sodium hydrate.

In conclusion, the authors desire to express their thanks to Messrs. W. M. Bradley, G. R. Tracy, and W. Valentine, who have assisted in the present work.

NEW HAVEN, FEBRUARY, 1897.

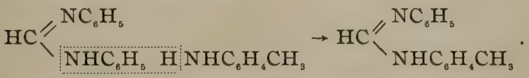
Contributions from the Sheffield Laboratory of Yale University.

LI.—ON THE NON-EXISTENCE OF FOUR METHENYLPHENYLPARATOLYLAMIDINES.

BY H. L. WHEELER.

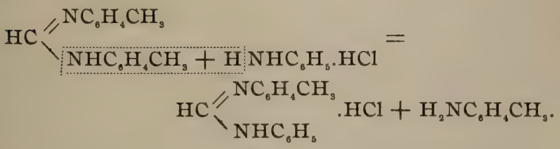
In the first number of the Journal für praktische Chemie for this year, Walther[1] describes the preparation of methenylphenylparatolylamidine by four different methods. Each method, according to him, gave a new amidine, and these amidines were supposed to be isomers. The methods he used and the compounds he claims to have obtained are as follows:

I. By heating methenyldiphenylamidine with *p*-toluidine a product was obtained which melted at 120°. He explains the formation of this as follows:



$$HC\begin{matrix} /\!\!/ NC_6H_5 \\ \backslash \boxed{NHC_6H_5\ \ H}NHC_6H_4CH_3 \end{matrix} \rightarrow HC\begin{matrix} /\!\!/ NC_6H_5 \\ \backslash NHC_6H_4CH_3 \end{matrix}.$$

II. By boiling an alcoholic solution of methenyldiparatolylamidine with aniline hydrochloride a product melting at 132° was obtained:



$$HC\begin{matrix} /\!\!/ NC_6H_4CH_3 \\ \backslash \boxed{NHC_6H_4CH_3 + H}NHC_6H_5.HCl \end{matrix} = HC\begin{matrix} /\!\!/ NC_6H_4CH_3 \\ \backslash NHC_6H_5 \end{matrix}.HCl + H_2NC_6H_4CH_3.$$

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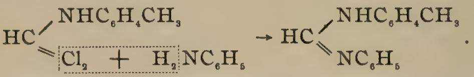
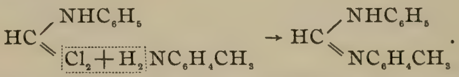
[1] Bd. 55, 41.

III. By treating a mixture of *p*-formtoluide with aniline and phosphorus trichloride a product melting at 98° was obtained. He states that the following amidine is expected to result here :



$$HC\begin{array}{l}\diagup NHC_6H_4CH_3\\ \diagdown\!\!\diagdown \boxed{Cl_2 \;+\; H_2}NC_6H_5\end{array} \rightarrow HC\begin{array}{l}\diagup NHC_6H_4CH_3\\ \diagdown\!\!\diagdown NC_6H_5\end{array}.$$

IV. Finally he states that by reversing the above and treating a mixture of formanilide and *p*-toluidine with phosphorus trichloride a reaction as follows must take place, or, in other words, that an amidine with the following structure must result :



$$HC\begin{array}{l}\diagup NHC_6H_5\\ \diagdown\!\!\diagdown \boxed{Cl_2 + H_2}NC_6H_4CH_3\end{array} \rightarrow HC\begin{array}{l}\diagup NHC_6H_5\\ \diagdown\!\!\diagdown NC_6H_4CH_3\end{array}.$$

Walther concludes that two of these amidines are structural isomers while the others are perhaps physical modifications or stereochemical isomers.

The existence of four isomeric methenylphenylparatolylamidines is theoretically possible and would therefore not be remarkable, but that these four should be formed separately in the above reactions is not in harmony with the general behavior of amidines, imide chlorides,[1] or imidoesters, and that these substances should act by direct double decomposition, as indicated above, seems incredible. Moreover, these results are not in harmony with the careful work of Pechmann[2] on the amidines. Pechmann has shown in several cases that only one amidine results, when prepared from imide chlorides, where two might be expected.[3]

The re-examination of the above products was therefore undertaken with the result that all attempts to confirm the statements of Walther were unsuccessful. In no case, by the first and second method, were products obtained that melted constantly at 120° or 132°. Products were obtained that melted near these temperatures, and corresponded otherwise with Walther's descriptions, but, when crystallized, they proved to be nothing but impure methenyldiphenylamidine and methenyldiparatolylamidine, respectively.

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[1] Most probably imide chlorides are to be considered in reactions III and IV and not amide chlorides.

[2] Ber. d. chem. Ges., **28**, 869 and 2362.

[3] It may be stated here that seven years ago while the author was engaged in a research on the isoanilides with Mr. W. J. Comstock, it was observed that the same amidine resulted when prepared from phenylformimidomethyl ester and metanitraniline or from metanitrophenylformimidomethyl ester and aniline. The products obtained by these different methods were identical in regard to melting-point and general behavior. The preparation of this amidine by only one method was given at that time, the intention being to examine the subject more thoroughly and the work had just been resumed when Pechmann's article appeared.

According to the third and fourth method apparently one and the same methenylphenylparatolylamidine was obtained. This did not melt at 98° nor at 102° when purified by repeated crystallizations, but more nearly at 103°.5 to 104°, when prepared by the third method, and at 103°.5 to 104°.5, or practically at 104°, when prepared by the fourth method. The products could not be distinguished in appearance and properties except by this slight difference in melting-points. This difference in complete melting is to be explained by the fact that when this amidine is prepared by the third method, under certain conditions, an impurity accompanies the chief product, which it is difficult or impossible to separate by crystallizing from ligroïn. This impurity is probably methenyldiparatolylamidine.

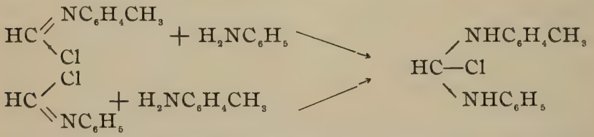
The amidine melting at about 103°.5 is the true methenylphenylparatolylamidine, since the same compound results from paratolylformimidomethyl ester and aniline.

Walther comments on the products obtained by the third and fourth methods, as follows: "Allein an der Verschiedenheit beider Körper ist nicht zu zweifeln; beim Umkrystallisiren derselben aus warmem Petroläther ist der Unterschied in ihrem Verhalten schon deutlich ausgeprägt: der Körper vom Schmelzp. 98° löst sich leichter und fält beim Abkühlen der Lösung sofort in weissen Nadeln aus, der Körper von Schmelzp. 102° geht schwerer in Lösung und setzt sich langsam in harten kleinen Prismen ab."

The products that I obtained by Walther's third and fourth method could be made to crystallize at will in the form of needles or prisms. In order to obtain the needle form, a strong ligroïn or petroleum ether is to be taken and this cooled rapidly. If the solutions are dilute or moderately dilute, and are slowly cooled, or if allowed to evaporate spontaneously, prisms are invariably obtained. Apparently the prisms are obtained more readily the purer the material. No difference in melting-point was observed between the needles and prisms when these forms were prepared from pure material. The difference in solubility of these forms is only apparent; the prisms are thicker, larger crystals, and therefore, of course, dissolve less *rapidly* than the finely divided slender needles.

Platinum double salts of the supposed new amidines were obtained by Walther in each case, but since these were obtained from impure material, nothing would be gained by examining these. Attention was directed therefore entirely to the amidines.

The formation of only one amidine in reactions III and IV shows that the reaction is not a direct double decomposition, but that it involves an addition and then a separation. For example, both imide chlorides formed from the formyl compounds add the base giving the same compound, *i. e.*, the hydrochloric acid salt of the amidine, and this naturally breaks down in one way, or chiefly in one way :



The above addition-product can separate hydrogen chloride in either of two ways according as the double bond in the free amidine is between the methenyl group and the aniline or the toluidine rest. These reactions, therefore, show nothing in regard to the structure of methenylphenylparatolylamidine.

The Product Obtained by the First Method.

The directions for the preparation of the amidine melting at 120° are somewhat indefinite. Walther states : " Wird Diphenylmethenylamidin mit 1 mol. freien *p*-Toluidins längere zeit erhitzt, so erhält man eine Abscheidung von Anilin. Das resultirende gemischte Amiden bildet shöne weisse Nadeln von Schmelzp. 120°."

No temperatures are given, nor is the solvent stated which was used in the purification (?) of the product. Attempts to prepare this amidine were made as follows: 1.2 grams methenyldiphenylamidine and 0.6 grams of paratoluidine were heated to 100° for about three days. The material on cooling then became a dark-colored semi-solid mass. It was dissolved in cold alcohol and precipitated with water, dried on a plate, and then crystallized from ligroïn. It separated finally in the form of white needles, as Walther states, but the different crystallizations melted about as follows:

I. 102°–110°
II. 117°
III. 120°-125°
IV. 125°–127°
V. 127°–129°
VI. 128°–131°
VII. 131°–133°
VIII. 131°–133°

In the next experiment a larger quantity of material was taken. 5.5 grams of methenyldiphenylamidine and 3.0 grams of paratoluidine were kept at about 80° for four days and nights. The black mass was then taken up in alcohol precipitated with water, dried, and boiled in ligroïn with animal charcoal. On crystallizing from ligroïn needles separated, and the following melting-points were obtained:

I. 100°–108°
II. 112°–115°
III. 115°–122°
IV. 121°–125°
V. 125°–129°
VI. 130°–132°
VII. 135°–136°
VIII. 135°–136°

The above results show that the product thus obtained is a mixture, and that the amidine crystallizing in white needles, as described by Walther, is undoubtedly impure methenyldiphenylamidine. The melting-point of this is given by various observers from 135°–140°. Other solvents besides ligroïn were tried but no amidine melting constantly at 120° was obtained. The product was readily soluble in alcohol, ether, carbon disulphide, benzene, and chloroform. It had the appearance and properties of methenyldiphenylamidine.

The Product Obtained by the Second Method.

According to the second method, by heating methenyldiparatolylamidine[1] with aniline hydrochloride for a half hour in alcoholic solution, an amidine melting at 132° should result. The solvent used in purifying is not stated.

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[1] In describing methenyldiparatolylamidine as new, Walther overlooks the fact that this amidine was obtained by Senier (Ber. d. chem. Ges., **18**, 2294). Later this amidine and also methenyldimetanitrophenylamidine (dinitrodiphenylformamidine) was described in This JOURNAL, **18**, 517, by Comstock and others.

An experiment to confirm this statement was undertaken as follows: 2.9 grams of methenyldiparatolylamidine and 1.7 grams of aniline hydrochloride were warmed in a small amount of alcohol for a half hour on the steam-bath. (If warmed for a longer time the amidine is decomposed and nothing separates.) On cooling a mass of needles separated. These were dissolved in alcohol and precipitated with dilute ammonia, dried, and crystallized repeatedly from ligroïn. The products from the successive crystallizations gave approximately the following melting-points:

I. 125°
II. 132°
III. 132°–136°
IV. 133°–137°
V. 135°–138°
VI. 137°–140°
VII. 137°–140°

A portion of the hydrochloride was crystallized four times from alcohol and then decomposed with ammonia. Thus obtained it melted at about 135°–136°. When the crude amidine was crystallized twice from absolute alcohol, in which it is quite soluble, it melted from 132°–135°.

In another experiment 5 grams of the amidine and 3 grams of aniline hydrochloride were taken. The hydrochloric acid salt resulting on warming this mixture was crystallized six times from absolute alcohol and then decomposed with dilute ammonia, the dry product melted not sharply at 133°. However, on crystallizing this once from considerable low-boiling ligroïn, it came down in the form of lozenges and flattened bunches of crystals, representing exactly methenyldiparatolylamidine when crystallized under the same conditions. In this form when dry it melted fairly well at 140°.

The above results show that the material obtained by this method, and melting at about 132° is a mixture which, when crystallized, gives methenyldiparatolylamidine.

The Products Obtained by the Third and Fourth Methods.

The third method consists in treating *p*-formtoluide with aniline and phosphorus trichloride. No details are given for the conversion of the reaction-product into the amidine. It is stated that from petroleum ether the amidine separates in needles melting at 98°.

An experiment according to this method, using the quantities given by Walther, was performed as follows: 5 grams *p*-formtoluide and 3.6 grams of aniline were mixed and treated with an excess of phosphorus trichloride.

A violent reaction took place and the mass solidified. The material was washed with water, taken up in alcohol, and precipitated with dilute ammonia, dried, and crystallized from petroleum ether as directed. It then separated in needles or prisms according to the conditions already stated in the introduction. The material, after one crystallization from petroleum ether, melted from 102°–103°, and showed no signs of melting at 98°. After four crystallizations from ligroïn the material melted from 103°.5–104°.

In another experiment 10 grams of *p*-formtoluide, melting at 52°, and 7.2 grams of freshly distilled aniline were mixed; then phosphorus trichloride was slowly added in excess. The product thus obtained was treated as in the previous experiment. The free amidine was crystallized sixteen times from petroleum ether. It separated in needles and prisms, and the following are some of the melting-points which were observed:

I.	97°.0– 97°.5	IX.	102°.0–102°.5	XIV.	103°.5–104°
III.	98°.0–100°	XI.	102°.5–103°	XV.	103°.5–104°
VI.	100°.5–101°.5	XIII.	103°.0–104°	XVI.	103°.5–104°

In another experiment a specimen of *p*-formtoluide was used which was carefully freed from all traces of *p*-toluidine, and which after several crystallizations from ether melted sharply from 53°–54°. This gave the same result as stated in the first experiment above.

Several attempts were made to prepare this amidine from specimens of crude *p*-formtoluide melting at 52°, and from which *p*-toluidine had not been removed by treating with dilute hydrochloric acid and water. In these cases products were obtained melting at about 85°, and in one of these cases the material was crystallized seven times from ligroïn without raising its melting-point above 86°. On the other hand, when pure *p*-formtoluide was used, even the crude product melted higher than this. The lowering of the melting-point in these cases is, therefore, due to the presence of *p*-toluidine in the *p*-formtoluide used.

The fact that the amidine prepared by the third method, and from pure materials, melts lower than when prepared by the fourth, is now readily explained as follows: The phosphorus trichloride decomposes a small part of the *p*-formtoluide into *p*-toluidine hydrochloride, and this, by taking part in the reaction, effects a contamination (probably methenyldiparatolylamidine) that is difficult or impossible to remove by repeated crystallizations. On the other hand, the conditions in the fourth method are different. In that case there is no *p*-formtoluide present to form methenyldiparatolylamidine, and, if the formyl compound is decomposed, aniline is separated, this then forms methenyldiphenylamidine, which is more soluble in petroleum ether than the chief product, the mixed amidine. Hence, the material prepared by the fourth method is more readily purified.

An experiment, according to the fourth method, gave the following result: 5 grams of formanilide and 4.8 grams of *p*-toluidine were mixed and treated precisely as in the above experiment. The product from petroleum ether came down in needles or prisms, and after four crystallizations melted from 103°.5–104°.5.

From the above results it is concluded that only one methenylphenylparatolylamidine exists. In conclusion, the author expresses his indebtedness to Mr. J. A. Hall, who has assisted him in the present work.

NEW HAVEN, CONN., March, 1897.

Contributions from the Chemical Laboratory of Case School of Appled Science.

XXV.—INVESTIGATIONS ON AMERICAN PETROLEUM.

ON THE COMPOSITION OF A SOUTH AMERICAN PETROLEUM.[1]

BY CHARLES F. MABERY AND ARTHUR S. KITTELBERGER.

It has long been known that large deposits of petroleum are to be found in various districts in South America, but beyond a limited use of the crude oil in lubrication, until recently no demand has been created for this petroleum. In the Argentine Republic are found heavy oils that deposit paraffin on distillation. In an examination of these oils by Engler and Ottin, hydrocarbons were found of the series $C_n H_{2n+2}$ and $C_n H_{2n}$; they are said to yield a good illuminating oil. The oil fields of Peru and Bolivia have long been known, and large quantities of petroleum products are here obtained. The most promising oil fields hitherto in South America are those of Venezuela, and those deposits are receiving more attention in the preparation of commercial products.

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[1] Presented to the American Academy of Arts and Sciences, October, 1896. Aid in the work described in this paper was given by the Academy from the C. M. Warren Fund for Chemical Research.—C. F. M.

The peculiar character of South American petroleum was brought to the attention of one of us (Mabery) in an examination which he was called upon to make by Mr. Horace M. Wilson, of Cambridge, Mass., who collected a specimen of oil while "prospecting" along the Magdalena River in the United States of Colombia. A few miles from the river, in a rocky section of country, he discovered oil oozing up through a pool of water from a fissure in the rocks below. Oil was also observed escaping in bubbles through the water in a brook, where it formed a beautiful green layer three yards square. These sources and another within a range of two thousand feet were the only ones observed in a distance of fifteen miles. The geological formations in this section consist of sandstones and shales tilted in nearly a horizontal position. At a distance of forty miles was a very large deposit of asphalt, hard and brittle like coal. About eighty gallons of this oil was collected at a rate of five gallons in twenty-four hours, of which the larger portion mixed with lard oil was used as a lubricator on car axles, for which it was found to be well adapted. Mr. Wilson brought home fifteen gallons of the oil, which was placed at our disposal for this examination.

The specific gravity of the crude oil was found to be 0.9480 at 20°. It is a high sulphur oil, as shown by the following determinations: (I), 0.70; (II), 0.66 per cent. It absorbed bromine equivalent to 12.09 per cent. It also contains a large quantity of nitrogen, as shown by the following determinations: (I), 0.321; (II), 0.315 per cent. A determination of ash in the crude oil was made, in which 29.1360 grams of the oil was burned, and the ash ignited until all carbon was consumed. The residue weighed 0.313 gram, equivalent to 0.011 per cent., or the same amount of ash as is obtained from Ohio crude oil.[1] The ash contains much iron, as shown by its brown color.

Determinations of carbon and hydrogen in the crude oil gave the following results:

	I.	II.
C	85.80	85.45
H	12.02	11.79

The crude oil was dark in color, thick and viscous, flowing very slowly at ordinary temperatures. In attempting to distil it under ordinary atmospheric pressure, nothing came over below 260°, and between this point and 345° it distilled in the following proportions, beginning with 290 cc.

	—310° 70 cc.	310°-345° 70 cc.
Specific gravity	0.8749	0.8615
Bromine-absorption	0.46	34.96

As the great increase in bromine-absorption shows, the distillate 310°–345° was badly cracked, and it had the very disagreeable odor of the worst decomposition-products of high petroleum distillates. The lower fraction had only the natural odor of an undecomposed distillate. Nothing could be distilled above 345°, and the residue was completely coked. In respect to the instability of its least volatile portions, this oil differs from any North American oil that has come under my observation (Mabery). It was therefore evident that another method of distillation must be resorted to with any hope of separating without decomposition the principal constituents.

In subjecting the crude oil to distillation *in vacuo* under 50 mm., the first distillate came over at 100°, and below 250° the following weights were collected from 14.5 kilos, after the fourth distillation. It cannot be assumed that the absence of more volatile constituents was the result of evaporation by exposure on the surface of the water where the oil was found, since it was collected as soon as it appeared. No doubt such volatile portions as constitute gasoline on long exposure under such circumstances would be lost, but no constituents, such as higher members of $C_n H_{2n+2}$, which do not appear in this oil.

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[1] Proc. Amer. Acad., **31**, 20.

	—130°	130°-135°	135°-140°	140°-150°	150°-155°	155°-160°	160°-165°
Grams	265	100	115	225	200	65	95
Sp. gr.					0.8706	0.8736	0.8747

	165°-170°	170°-175	175°-180°	180°-185°	185°-190°	190°-195°
Grams	130	130	70	125	115	155
Sp. gr.	0.8784	0.8806	0.8846	0.8858	0.8867	0.8884

	195°-200°	200°-205°	205°-210°	210°-215°	215°-220°	220°-225°
Grams	140	165	95	110	100	145
Sp. gr.	0.8926	0.8947	0.8964	0.8989	0.9020	0.9045

	225°-230°	230°-235°	235°-240°	240°-245°	245°-250°	+250°
Grams	145	150	100	93	75	130
Sp. gr.	0.9078	0.9113	0.9137			

Distillation of the fractions below 150° amounting to 700 grams was continued under atmospheric pressure, collecting within the limits of two degrees. After five distillations, ten in all from the beginning, heaps collected at 170°, 190°, and 212°, although in small quantities. The distillation could not be pushed too far on account of decomposition. The fraction 170°–172° (730 mm.) gave the following percentages of carbon and hydrogen:

0.1456 gram of the oil gave 0.4556 gram CO_2, and 0.1864 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Found.
C	85.71	85.33
H	14.29	14.23

Unfortunately there was not enough of this fraction to determine its specific gravity. A determination of sulphur gave 0.05 per cent. Its bromine-absorption was found to be 3.5 per cent. No other heap appeared in the distillates below 190°. At 190°–192° more collected, evidently corresponding to a hydrocarbon boiling at 196°. A determination of the specific gravity of this distillate gave 0.8381. It absorbed bromine amounting to 3.56 per cent. A determination of sulphur gave 0.10 per cent. A combustion gave the following percentages of carbon and hydrogen :

I. 0.1696 gram of the oil gave 0.5332 gram CO_2. The water was lost.

II. 0.1542 gram of the oil gave 0.4846 gram CO_2, and 0.1912 gram H_2O.

	Calculated for $C_{11}H_{22}$.	Found. I.	II.
C	85.71	85.73	85.69
H	14.29	....	13.78

The distillate was treated with a mixture of nitric and sulphuric acids, then with fuming sulphuric acid. In the first treatment, a very small quantity of a nitro compound separated as an oil, showing a trace of an aromatic hydrocarbon. The fuming acid produced no appreciable action.

A determination of carbon and hydrogen in this product gave the following results :

0.1618 gram of the oil gave 0.5019 gram CO_2, and 0.2087 gram H_2O.

	Calculated for $C_{11}H_{22}$.	Found.
C	85.71	85.47
H	14.29	14.33

A determination of the specific gravity of the oil after this treatment gave 0.8333. Besides a very small proportion of aromatic hydrocarbon $C_n H_{2n-6}$, evidently this distillate is composed of a single body, although analysis alone is not sufficient to determine whether its composition is represented by the formula $C_{11}H_{22}$ or $C_{12}H_{24}$.

Above 192° no distillates collected in appreciable amounts below 210°. At 212°–214° a larger quantity collected, evidently corresponding to a hydrocarbon boiling at 216°, which has been found in other oils. A determination of its specific gravity gave 0.8483. It absorbed bromine equivalent to 4.29 per cent., and contained 0.04 per cent. of sulphur. A determination of the carbon and hydrogen gave the following percentages:

0.1555 gram of the oil gave 0.4887 gram CO_2, and 0.1992 gram H_2O.

	Calculated for $C_{12}H_{24}$.	Found.
C	85.71	85.72
H	14.29	14.23

A small quantity of nitro product was formed, when this distillate was treated with nitric and sulphuric acids, and fuming sulphuric acid then removed more of the nitro compound from the oil. The oil shaken with sodic hydrate imparted a yellow color to the alkaline solution ; it was then redistilled for analysis :

0.1590 gram of the oil gave 0.4984 gram CO_2, and 0.2037 gram H_2O.

	Calculated for $C_{11}H_{22}$.	Found.
C	85.71	85.48
H	14.29	14.23

A determination of the specific gravity of the oil after treatment with acids gave 0.8484, the same value as was obtained for the crude distillate. It was therefore evident that this petroleum consists mainly of a single series of hydrocarbons, with a mere trace of aromatic hydrocarbons $C_n H_{2n-6}$. What this series is does not appear from these results, at least so far as its relation to the series of hydrocarbons hitherto discovered in petroleum. In the proportions of carbon and hydrogen, the series $C_n H_{2n}$, is indicated. Neither the crude oil nor any of these distillates deposit paraffin, even at low temperatures. The higher distillates are thick and viscous, light yellow in color, and unquestionably are undecomposed constituents of the crude oil.

With nitric and sulphuric acids the constituents described in this paper are as slightly affected as are the naphtenes in the Russian oil. This fact, together with the results of analysis corresponding to the series $C_n H_{2n}$, and the high specific gravity, point to a similar composition for these bodies, and the small proportion of the crude oil distilling below 220° seems, therefore, to be composed almost exclusively of naphtenes, which is the first instance of an American petroleum having been found containing these hydrocarbons in any considerable quantity. The higher distillates from this petroleum will receive further attention in connection with the corresponding portions of other American oils.

Having at hand a specimen of petroleum from Oregon, resembling the heavier California products, with a specific gravity nearly the same as that of the South American oil described above, it seemed of sufficient interest to submit it to an examination in connection with that of the South American oil. The crude oil was very thick and dark, with a specific gravity of 0.9597 at 20°. Like the California oils, as shown by Peckham, it contains a large percentage of nitrogen compounds. A Kjeldahl determination gave 0.868 per cent. of nitrogen. This is also a high sulphur oil, as shown by a combustion which gave 1.19 per cent. of sulphur. It is also a high carbon oil; a combustion gave 86.06 per cent. of carbon, and 11.87 per cent of hydrogen. A very small proportion distils under atmospheric pressure, without decomposition; even under diminished pressure, the amounts distilling below 250° are small.

In attempting to separate the constituents of this oil from the distillate first collected *in vacuo*, the portions below 250°, about the same in amount as the corresponding distillates from the South American oil, were carried through ten distillations under atmospheric pressure, which brought together larger quantities at 169°–170°, 190°–191°, and 212°–214°. The portions collected at 85°–150° in the first distillation gave as its specific gravity at 20°, 0.8755; the distillate 150°–225°, 0.9038; and the distillate 225°–250°, 0.9271. After the tenth distillation, the fraction 170°–171° gave as its specific gravity, 0.8200; the fraction 189°–190°, 0.8330; and the fraction 212°–214°, 0.853. A combustion of the fraction 189°–190° gave the following percentages of carbon and hydrogen:

0.1510 gram of the oil gave 0.4757 gram CO_2, and 0.1835 gram H_2O.

C	85.90
H	13.51

After purification with nitric and sulphuric acids, the composition of this oil was not essentially changed:

0.1484 gram of the oil gave 0.4643 gram CO_2, and 0.1839 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.71	85.33
H	14.29	13.77

The fraction 212°-214°, without purification, gave the following results :

0.1457 gram of the oil gave 0.4625 gram CO_2, and 0.1757 gram H_2O.

C	86.46
H	13.40

By treatment with a mixture of nitric and sulphuric acids, and then with fuming sulphuric acid, this distillate was only slightly affected :

0.1343 gram of the oil gave 0.4231 gram CO_2, and 0.1677 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.71	85.90
H	14.29	13.88

Unfortunately the quantities of these distillates were too limited to permit of further examination. The principal object, however,—to ascertain whether any members of the series $C_n H_{2n+2}$ were present at all, or the aromatic hydrocarbons $C_n H_{2n-6}$ in more than minute proportions,—was attained. Evidently the main body of this oil is composed of a series with less hydrogen than the former and more than the latter. The oil distils in such small quantities, even *in vacuo*, below 220°, that it will be interesting to ascertain the composition of the distillates above this point.

Contributions from the Chemical Laboratory of the Lehigh University.

IV.—THE ACTION OF CERTAIN ALCOHOLS ON *ASYM*-METADIAZOXYLENESULPHONIC ACID.

By W. B. Shober and H. E. Kiefer.[1]

The starting-point in this investigation was the preparation of *a*-metaxylidinesulphonic acid. The directions given by Jacobson and Ledderboge[2] were followed. A mixture of 300 cc. of *a*-metaxylidine (Kahlbaum's preparation), boiling at

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[1] Dissertation submitted to the Faculty of the Lehigh University, for the Degree of Doctor of Philosophy by Herman Eugene Kiefer, June, 1896.

[2] Ber. d. chem. Ges., **16**, 193.

211°–212°, 150 cc. concentrated sulphuric acid, and 300 cc. of fuming sulphuric acid, was heated in a sulphuric-acid bath for three hours at a temperature of 140°–150°. On cooling the reaction-mixture solidified; it was slightly warmed and poured into 4 liters of ice-water. The sulphonic acid separating out was filtered off with the aid of suction; the pasty mass was then kneaded with an excess of barium carbonate, boiled with water and filtered while hot through muslin. The filtrate was treated with a sufficient amount of potassium carbonate to precipitate the barium, filtered and evaporated to crystallization. The potassium salt was obtained in good crystals of a light yellow color.

Diazotization of the Potassium Salt.

The directions given by Sartig[1]—diazotization with potassium nitrite in hydrochloric-acid solution—were followed exactly, but satisfactory results could not be obtained; another method was therefore tried. The potassium salt obtained, as above described, was converted into the free acid by treatment with hydrochloric acid. The free acid was washed on the filter with much cold water and dried on porous plates.

Ten grams of the dry xylidinesulphonic acid was converted into a thick paste with water, and nitrous fumes, from arsenic trioxide and nitric acid, were passed into it until the mass dissolved; this occurred in fifteen minutes. Four volumes of cooled alcohol was then added and the mixture allowed to stand fifteen minutes in an ice-salt mixture. The diazo compound was filtered off, washed with alcohol, then ether, and dried in the air on filter-paper; the dried compound weighed 9 grams. It was afterwards boiled with absolute alcohol under pressure; the decomposition was complete, there being no residue, thus showing that the diazo compound was not contaminated with any xylidinesulphonic acid which had escaped diazotization.

The theoretical yield of the diazo compound from 10 grams of the amido acid is 10.6 grams. We obtained 9 grams, or 94 per cent. of the theoretical.

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[1] Ann. Chem. (Liebig), **230**, 337.

Action of Methyl Alcohol on a-Metadiazoxylenesulphonic Acid at the Atmospheric Pressure.

The diazo compound was made by the method just described. The methyl alcohol used in this and the following experiments was Kahlbaum's purest preparation. It was allowed to stand over chemically pure lime several weeks before it was used. The two substances were placed in a flask, to which a reflux-condenser was attached, and heated on a water-bath. Decomposition began almost immediately, resulting in the formation of a dark, yellowish liquid. The excess of alcohol was distilled off, the resulting oily residue diluted with water, and neutralized with barium carbonate. The barium salt was converted into the potassium salt, this into the sulphon chloride and finally into the amide. An attempt was made to crystallize the amide from water, but it was unsuccessful, owing to the great insolubility of the compound; the proper solvent is alcohol. The amide was boiled with animal charcoal in alcohol and recrystallized several times. Two compounds were found, one melting at 136°, which is the xylenesulphonamide; another, melting at 190°, which, as shown by the analysis given below, is the amide of methoxyxylenesulphonic acid. The latter compound was formed in much larger quantity.

Action of Methyl Alcohol on the Diazo Compound at a Pressure of 400 mm. of Mercury.

The substances were placed in a pressure-flask, to which was attached a manometer. Upon applying heat, the reaction began almost immediately and was completed in thirty minutes. The alcohol was distilled off, and from the oily residue crystals of the free acid separated out on standing. These were dissolved by adding water; the acid liquid was neutralized with barium carbonate. The barium salt was converted into the potassium salt from which the chloride and amide were prepared. Two amides were again found; one melting at 190° and the other at 137°. The quantity of the latter was very small.

Action of Ethyl Alcohol on the Diazo Compound at Atmospheric Pressure.

Sartig[1] treated the diazo compound obtained by diazotizing the potassium salt in acid solution, with alcohol at the ordinary pressure. He found that the alcohol dissolved the diazo compound, but states that no decomposition took place on boiling. Our results are at variance with this statement.

The diazo compound and absolute alcohol were placed in a flask, to which a reflux-condenser was attached. The experiment was carried out in the same manner as the preceding ones. Two amides were formed as before, one melting at 137° and the other at 169°. The hydrogen amide (melting-point 137°) was formed in smaller quantity than the other.

In order to be certain of the identity of the amide melting at 169°, a sulphur determination was made with the following result :

0.2412 of amide gave 0.2453 gram of barium sulphate (Carius' method) corresponding to 13.98 per cent. of sulphur. The theory for sulphur in ethoxyxylenesulphonamide requires 13.99 per cent. This result, taken in connection with the melting-point, 169°, was deemed sufficient to characterize the compound. Moody[2] gives the melting-point 169°–170°.

Action of Ethyl Alcohol on the Diazo Compound at a Pressure of 360–380 mm. of Mercury.

The compounds were placed in the pressure-flask and heat applied. Reaction began at once and was complete after thirty-five minutes. The reaction-product was treated as in the preceding experiments. Two amides were again found ; the quantity of the hydrogen amide was very small.

Sartig[3] treated the diazo compound with absolute alcohol at a pressure of 360 mm. of mercury. He says : "The diazo compound decomposes on heating with absolute alcohol under a pressure of 360 mm. of mercury, but not with the formation of xylenesulphonic acid, but of ethoxyxylenesulphonic acid."

Since the hydrogen compound—xylenesulphonic acid—is formed in such small quantity, it is probable that Sartig overlooked its presence. He prepared, analyzed and described the barium salt, $(C_6H_2.CH_3.CH_3.OC_2H_5.SO_3)_2Ba+3H_2O$. It crystallizes in white microscopic leaflets, moderately soluble in water and in alcohol.

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[1] Ann. Chem. (Liebig), **230**, 337.

[2] Proc. Chem. Soc., 1891, 189.

[3] *Loc. cit.*

We prepared the potassium salt which crystallizes in leaflets; it is easily soluble in water, more difficultly soluble in alcohol. Its composition was not determined.

Moody[1] obtained the same ethoxyxylenesulphonic acid by boiling the diazo compound with "dehydrated methylated spirit." This result does not agree with that obtained by Sartig. Since Moody makes no reference to pressure, it is assumed that he effected the decomposition at the ordinary pressure. Sartig, working under the same conditions except that he used absolute alcohol, found that no decomposition took place. Judging from Moody's experiments, our own and others on record, it is probable that Sartig's observation is incorrect. It is possible, however, that the diazo compound may be more susceptible to the action of methylated spirit than to that of absolute alcohol.

Action of Ethyl Alcohol on the Diazo Compound at a Pressure of 900 mm. of Mercury.

The experiment was conducted in the usual manner: 4.2 grams of the diazo compound and 100 cc. of absolute alcohol were placed in the pressure-flask and heated. The decomposition was complete in a short time. The reaction-product was treated as before. Two amides were found; one melting at 160°, the ethoxyamide, and the other at 137°. The latter was formed in minute quantity.

Action of Propyl Alcohol on the Diazo Compound at a Pressure of 820–840 mm. of Mercury.

The propyl alcohol used was Kahlbaum's preparation (boiling-point 96°). It was dehydrated over lime. A mixture of 4.3 grams of the diazo compound and 100 cc. of propyl alcohol was treated in the usual way. The decomposition was complete in thirty minutes. Two amides were formed: one melting at 137°; the other at 145°. This latter was formed in great excess. As shown by the analysis given below, it was propoxyxylenesulphonamide.

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[1] Proc. Chem. Soc., 1891, 189.

A Study of the Asym-metamethoxyxylenesulphonic Acid and Some of its Derivatives.

The barium salt obtained by decomposing *a*-metadiazoxylenesulphonic acid with methyl alcohol and neutralizing the reaction-product with barium carbonate, was divided into two portions. One portion was converted into the corresponding amide. An analysis (given below) proved it to be the amide of methoxyxylenesulphonic acid. The other portion was dissolved in water and treated with just enough sulphuric acid to precipitate all the barium; the barium sulphate was filtered off and the filtrate concentrated. On standing, the free methoxyxylenesulphonic acid separated out in a mass of brownish needles. By boiling with animal charcoal and recrystallizing several times from water, the crystals were obtained free from color.

The acid decomposes on heating; it is very soluble in water, alcohol, and ether; difficultly soluble in pure benzene, from which it crystallizes in microscopic needles.

Potassium Salt, $C_6H_2.\overset{1}{C}H_3.\overset{3}{C}H_3.O\overset{4}{C}H_3.S\overset{6}{O}_3K + \frac{1}{2}H_2O$. — This salt was made by treating the barium salt with potassium carbonate, filtering off the barium carbonate, and concentrating the filtrate to crystallization. An analysis for potassium and water gave the following results:

0.08495 gram of the substance heated to 160° for one hour lost 0.00315 gram.

0.08495 gram of the substance gave 0.028 gram of potassium sulphate.

	Calculated for $C_9H_{11}SO_4K + \frac{1}{2}H_2O$.	Found.
K	14.79	14.86
$\frac{1}{2}H_2O$	3.41	3.70

The potassium salt is extremely soluble in water, readily soluble in dilute alcohol, more difficultly soluble in ordinary alcohol. From a concentrated water solution it crystallizes in very fine, yellow needles; from dilute alcohol in larger needles.

Barium Salt, $(C_6H_2.\overset{1}{C}H_3.\overset{3}{C}H_3.O\overset{4}{C}H_3.\overset{6}{S}O_3)_2Ba + 4H_2O$.—This salt was obtained by treating the free acid with an excess of barium carbonate, filtering off the excess, and evaporating to crystallization.

An analysis for barium and water gave the following results :

0.1709 gram of the salt was heated for one and a half hours at 150° ; the loss in weight was 0.0191 gram.

0.1709 gram of the salt gave 0.0615 gram of barium sulphate.

	Calculated for $C_{18}H_{22}S_2O_8Ba + 4H_2O$.	Found.
Ba	21.46	21.17
$4H_2O$	11.25	11.18

The salt is readily soluble in water, from which it crystallizes in yellow, warty masses or in clusters of ill-defined needles ; it is more difficultly soluble in 80-per cent. alcohol. From the alcoholic solution it crystallizes in small lustrous, yellow plates.

Copper Salt, $(C_6H_2.\overset{1}{C}H_3.\overset{3}{C}H_3.O\overset{4}{C}H_3.\overset{6}{S}O_3)_2Cu + 4H_2O$.—This compound was prepared by adding copper sulphate to a solution of the barium salt. A determination of the water of crystallization gave the following result :

0.47952 gram of the salt lost 0.0597 gram on being heated for two hours at 160°.

	Calculated for $C_{18}H_{22}S_2O_8Cu + 4H_2O$.	Found.
$4H_2O$	12.73	12.45

The hydrous crystals are apple-green in color ; on being dehydrated they become yellow. The salt is soluble in water, less soluble in alcohol ; from alcohol it crystallizes in fine needles.

A *Zinc* and a *Sodium Salt* were also prepared. Both are easily soluble in water and less soluble in alcohol. They were not analyzed.

The Amide, $C_6H_2.\overset{1}{C}H_3.\overset{3}{C}H_3.O\overset{4}{C}H_3.\overset{6}{S}O_2NH_2$.—This compound was prepared in the usual way from the potassium salt. An analysis gave the following results :

0.2283 gram of the substance gave 0.4216 gram of carbon dioxide.

0.2493 gram of the substance gave 0.1321 gram of water.

0.2057 gram of the substance gave 0.22673 gram of barium sulphate, Carius' method.

0.8735 gram of the substance gave 0.06615 gram of ammonia (Kjeldahl-Gunning Method).

	Calculated for $C_9H_{13}SNO_3$.		Found.	
			I.	II.
C_9	107.73	50.20	50.36	...
H_{13}	13.00	6.05	....	5.90
S	31.98	14.90	15.14	...
N	14.01	6.52	6.23	...
O_3	47.88	....	....	...
	214.60	100.00		

The amide is insoluble in cold water, very difficultly soluble in hot water, soluble in alcohol. From its water solution it crystallizes in very fine, white needles; from an alcoholic solution in coarser needles. Several determinations gave 190° as the melting-point.

A Study of Asym-Propoxyxylenesulphonic Acid and Some of Its Derivatives.

The free acid was obtained as follows: Asym-metadiazoxylenesulphonic acid was decomposed in the presence of anhydrous propyl alcohol at a pressure of 850-900 of mm. of mercury. The resulting brownish-red liquid was heated until the alcohol distilled off; then diluted with water, and neutralized with barium carbonate. The excess of barium carbonate and the barium sulphate were filtered off, the filtrate was boiled with animal charcoal, filtered, and evaporated. On standing, crystals of the barium salt were deposited; these crystals were dissolved in water and the solution was treated with a quantity of sulphuric acid sufficient to precipitate all the barium. The barium sulphate was filtered off, and the filtrate evaporated to crystallization. Large tablets, apparently orthorhombic, were deposited.

The acid is very soluble in water and in alcohol. From the alcoholic solution it crystallizes in fine needles. The acid itself was not analyzed, but an analysis of the amide derived from it is given below.

Barium Salt, $(C_6H_2.\overset{1}{C}H_3.\overset{3}{C}H_3.O\overset{4}{C}_3H_7.S\overset{6}{O}_3)_2Ba + 3H_2O$.—The barium salt was prepared by neutralizing the free acid with chemically pure barium carbonate. The excess of barium carbonate was filtered off and the filtrate evaporated to crystallization.

Determinations of barium and water gave the following results:

0.30805 gram of the substance dried in the air for twenty-four hours and then heated to 150° for one hour, lost 0.02385 gram and gave 0.1042 gram of barium sulphate.

0.1746 gram of the substance under the same conditions lost 0.0132 gram and gave 0.0595 gram of barium sulphate.

	Calculated for $C_{22}H_{30}S_2O_8Ba + 3H_2O$.	Found. I.	II.
Ba	20.25	19.89	20.04
$3H_2O$	7.97	7.74	7.56

The barium salt is moderately soluble in water and in alcohol. From the water solution it crystallizes in clusters of small, glistening needles, faintly yellow; from the alcoholic solution clusters of small plates are deposited.

Potassium Salt, $C_6H_2.CH_3.CH_3.OC_3H_7.SO_3K + H_2O$.—The potassium salt was prepared by treating the barium salt with potassium carbonate, filtering off the barium carbonate, and evaporating the filtrate to crystallization. The crystals were dried in the air; a determination for potassium and water gave the following results:

0.24838 gram of the salt heated at 120° for three hours lost 0.01533 gram and gave 0.0728 gram of potassium sulphate.

	Calculated for $C_{11}H_{15}SO_4K + H_2O$.	Found.
K	13.32	13.15
H_2O	5.99	6.17

The salt is easily soluble in water and alcohol. It crystallizes in small yellow needles or in quadratic tablets.

Zinc Salt, $(C_6H_2.\overset{1}{C}H_3.\overset{3}{C}H_3.O\overset{4}{C}_3H_7.S\overset{6}{O}_3)_2Zn + 5H_2O$.—This salt was prepared from the barium salt by treating it with zinc sulphate; the barium sulphate was filtered off and the filtrate evaporated to crystallization. The crystals were dried in the air for twelve hours and over sulphuric acid for twelve hours. A partial analysis gave the following results:

0.19007 gram of the substance on heating to 150° for one hour lost 0.02605 gram and gave 0.04567 gram of zinc sulphate:

	Calculated for $C_{22}H_{30}S_2O_8Zn + 5H_2O$.	Found.
Zn	10.18	9.72
$5H_2O$	14.03	13.70

The salt is very soluble in water, less soluble in alcohol. It crystallizes in fine transparent leaflets or in columns of a slightly yellow color.

The Amide, $C_6H_2.\overset{1}{C}H_3.\overset{3}{C}H_3.O\overset{4}{C}_3H_7.S\overset{6}{O}_2NH_2$.—This compound was prepared from the potassium salt in the usual way: An analysis of it gave the following results:

0.09889 gram of the substance gave 0.1956 gram of carbon dioxide and 0.0667 gram of water.

0.2064 gram of the substance 0.1987 gram of barium sulphate (Carius' method).

	Calculated for $C_{11}H_{17}SO_3N$.		Found.
C_{11}	131.67	54.29	53.93
H_{17}	17.00	7.01	7.47
N	14.01	....	....
S	31.98	13.18	13.22
O_3	47.88	....	....
	242.54		

The amide is very difficultly soluble in water, easily soluble in alcohol. It crystallizes in fine needles, melting at 146°.

Oxidation of Asym-Metamethoxyxylenesulphonamide.

In view of the many interesting results obtained by Remsen and other investigators on oxidizing aromatic sulphonamides, it was deemed advisable to study the behavior of *a*-metamethoxyxylenesulphonamide on oxidation.

In order to obtain a sufficient quantity of the amide, successive quantities of the diazo compound were decomposed with methyl alcohol at a pressure of 800–900 mm. of mercury, and the reaction-product treated as described above. A different method of diazotization was employed, however. While the method described above usually gave good results, at times due to a slight variation in temperature or in the rapidity of the current of nitrous fumes, the entire quantity of the diazo-compound would decompose. We, therefore, tried another method. The dry metaxylidinesulphonic acid was ground to a very fine powder and suspended in ordinary alcohol, into which cooled nitrous fumes were passed until the substance became granular; the vessel containing the alcohol was surrounded by an ice-salt mixture. By this method we were enabled to convert 100 grams of the amido acid into the diazo compound in three hours; it has the disadvantage, however, that at times a small portion of the acid escapes diazotization.

Ten grams of asym-metamethoxyxylenesulphonamide was ground to a fine powder and triturated with water until a paste was formed: this was transferred to a 2-liter flask containing 1.5 liters of water and 40 grams potassium permanganate. The flask was placed *in* a water-bath, the temperature of which was maintained at 90°–96° for twenty hours. At the expiration of this time the flask was removed, a few drops of alcohol added, and allowed to stand until the manganese compounds had settled. The clear colorless solution was decanted and filtered; the residue was washed with hot water and filtered. The filtrates were poured together, evaporated to one-fourth their volume, and allowed to stand twelve hours, in order that any unoxidized amide might crystallize out. In every experiment a small quantity of the amide was found unoxidized. This was filtered off and an excess of hydrochloric acid added to the filtrate, which was then allowed to stand twelve hours. Long, acicular, white crystals, melting with decomposition at 236°–238°, separated out; these were filtered off, the filtrate concentrated and again allowed to stand for twelve hours. Two kinds of crystals were deposited—those just mentioned and flat, white, flaky crystals melting at 270°–275° with decomposition; they were separated by fractional crystallization.

An analysis of the compound melting at 236°–238° gave the following results :

0.6582 gram of the substance heated for twenty-two hours at a temperature of 120°–140° lost 0.0435.

1.2256 grams of the substance heated for thirteen hours at 150°–160° lost 0.084 gram.

0.2325 gram of the dried substance gave 0.3743 gram carbon dioxide and 0.0962 gram of water.

0.4106 gram of the substance gave 0.022911 gram of nitrogen.

0.4272 gram of substance gave 0.023936 gram of nitrogen (Kjeldahl-Gunning method).

0.2211 gram of the substance gave 0.2083 gram of barium sulphate (Carius' method).

Calculated for $C_6H_2.CH_3.COOH.OCH_3.SO_2NH_2 + H_2O$.			Found.	
C_9	107.73	44.05		43.91
H_{11}	11.00	4.49		4.59
O_6	79.80	....		....
S	31.98	13.08		12.94
N	14.01	5.72	5.58	5.60
	244.52	100.00		
H_2O	17.96	6.84	6.61	6.84
	262.48			

The compound, therefore, appears to be methoxysulphaminetoluic acid containing one molecule of water; the carboxyl is probably in the meta position to the sulphamine group. The substance crystallizes in fine needles; it is difficultly soluble in water and ether, more easily soluble in alcohol (melting-point 236°–238°).

Barium Salt, $(C_6H_2.CH_3.OCH_3.SO_2NH_2COO)_2Ba + 7H_2O$. —This salt was prepared by boiling the free acid with chemically pure barium carbonate ; the excess of the latter was filtered off and the filtrate evaporated. Attempts to obtain well-formed crystals from the water solution were unsuccessful. From a 50-per cent. alcohol flat, tabular crystals were obtained, a partial analysis of which gave the following results :

0.3723 gram of the substance dried in the air for one and a half hours lost 0.061 gram on being heated to 110° for three hours.

0.3205 gram of the dried salt gave 0.1199 gram of barium sulphate.

	Calculated for $C_{18}H_{22}S_2N_2O_{10}Ba + 7H_2O$.	Found.
Ba	21.93	22.04
$7H_2O$	16.76	16.38

Calcium Salt, $(C_6H_2.CH_3.OCH_3.SO_2NH_2.COO)_2Ca+7H_2O$.—This salt was prepared by boiling the free acid with chemically pure calcium carbonate; the excess of carbonate was filtered off and the filtrate evaporated. As was the case with the barium salt, we were unable to obtain good crystals from the water solution. From 50-per cent. alcohol, flat tabular crystals were deposited. A partial analysis gave the following results:

	Calculated for $C_{18}H_{22}S_2N_2O_{10}Ca + 7H_2O$.	Found.
Ca	7.59	7.70
H_2O	19.60	19.53

A *sodium salt* and a *potassium salt* were also prepared; they are exceedingly soluble in water from which they do not crystallize well. They were not analyzed. The substance melting at 270°–275° contains no nitrogen. Two determinations for carbon gave, respectively, 34.159, and 34.16 per cent.

SOUTH BETHLEHEM, PENNA.,
June, 1896.

THE ACTION OF ETHYLIC OXALATE ON CAMPHOR. (II.)

BY J. BISHOP TINGLE.

Introduction.

It has been shown by Claisen and his students[1] that under the influence of sodium ethylate, ketones of the formula $R.CO.CH_3$ or $R.CO.CH_2R$ condense with ethylic oxalate and similar compounds, forming ethereal salts of 1,3-diketo acids—thus acetone and ethylic oxalate yield ethylic acetone oxalate, $CH_3.CO.CH_2.CO.CO.OC_2H_5$. Ketones of the formula

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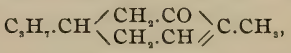
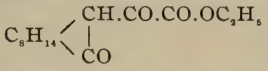
[1] Ann. Chem. (Liebig), **281**, 306.

$R.CO.CHR_2$ do not react in this manner, and W. Wislicenus found[1] that the corresponding acids $R_2.CH.CO.OC_2H_5$ also fail to replace the hydrogen of the methine group by acid radicles. At the time this work was commenced, in 1889, camphor was usually represented by Kekule's expression,



$$C_3H_7.CH\left\langle\begin{array}{l}CH_2.CO\\ CH_2.CH\end{array}\right\rangle C.CH_3,$$

the position of the double bond and also of the carbonyl group being stated by himself as somewhat doubtful. The attempt was therefore made to condense camphor and ethylic oxalate, and the resulting product, ethylic camphoroxalate,



$$C_8H_{14}\left\langle\begin{array}{l}CH.CO.CO.OC_2H_5\\ \;|\\ CO\end{array}\right.$$

was, together with some of its derivatives, briefly described in 1890.[2] Circumstances compelled the work to be suspended, and it has only recently been found possible to prosecute it further. During the past few years the constitution of camphor has received much attention from various chemists, including Von Baeyer, W. A. Noyes, Tiemann, and Collie; the formulæ for this substance that have perhaps attracted most notice being those of Bredt, Tiemann, and Collie,[3] but as these all recognize the presence in the molecule of the —$CH_2.CO$— group, this part of the work has lost in interest. On the other hand, a controversy has sprung up between Nef, Claisen, and others, as to the constitution of the 1,3-diketones and keto-acids; tthe latter[4] regards them as essentially true diketones, except possibly where two isomeric forms of the same compound are known, whilst the former[5] considers that he has proved them to be unsaturated hydroxy derivatives with a constitution corresponding with that first suggested by Geuther for ethylic acetoacetate; *viz.*, $CH_3.C.OH : CH.CO.OC_2H_5$. The compounds chiefly investigated from this point of view, both by Claisen and Nef, all contain strongly negative groups, such as $CH_3.CO$ and C_6H_5CO; the radicle—$CO.OC_2H_5$—is comparatively feeble in this respect, as Bishop, Claisen, and Sinclair have shown.[1] Since the camphyl radicle is also but very feebly negative, and has a relatively great mass (= 151), it appeared possible that the further study of ethylic camphoroxalate might throw light on the constitution of this class of bodies, and the work has therefore been recently resumed. At present the results hardly warrant any strong assertions for or against either constitution, but it appears desirable to place on record the work already done, so as to reserve the field for further study.

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[1] Am. Chem. (Liebig), **246**, 329 and 339.

[2] J. Chem. Soc., **57** (1890), 652.

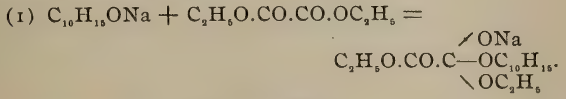
[3] Comp. W. A. Noyes: This JOURNAL, **18**, 1.

[4] Ann. Chem. (Liebig), **277**, 162.

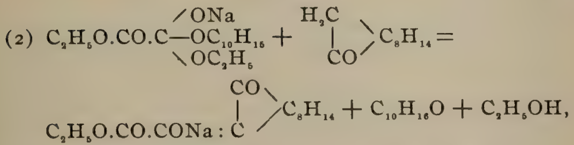
[5] *Ibid*, **266**, 52; **276**, 200; **277**, 59.

Theoretical.

The formation of ethylic camphoroxalate occurs most readily under the influence of sodium, the sodium camphor acting like sodium ethylate ; according to Claison's view[2] the reaction occurs in two stages :

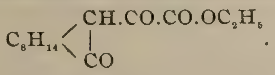
(1)


$$C_{10}H_{15}ONa + C_2H_5O.CO.CO.OC_2H_5 = C_2H_5O.CO.C\begin{array}{l}\diagup ONa\\ -OC_{10}H_{15}.\\ \diagdown OC_2H_5\end{array}$$

(2)


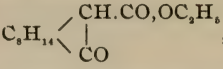
$$C_2H_5O.CO.C\begin{array}{l}\diagup ONa\\ -OC_{10}H_{15}\\ \diagdown OC_2H_5\end{array} + \begin{array}{l}H_2C\\ \quad|\\ CO\end{array}\!\!\!\!\!>C_8H_{14} = C_2H_5O.CO.CONa : \begin{array}{l}CO\\ \;|\\ C\end{array}\!\!\!\!>C_8H_{14} + C_{10}H_{16}O + C_2H_5OH,$$

the sodium salt when acidified yielding the free ketone



$$C_8H_{14}<\begin{array}{l}CH.CO.CO.OC_2H_5\\ \;|\\ CO\end{array}.$$

The hydrogen, liberated during the formation of sodium camphor, reduces a portion of the free camphor to borneol.

Ethylic camphoroxalate offers a rather remarkable contrast to formylcamphor, the latter, as Claison, Bishop, and Sinclair have shown (*loc. cit.*), is a very strong acid and readily forms an anhydride, etc., but the former does not appear to form a copper salt ; it is quickly decomposed when heated, and in presence of alkali is rapidly hydrolyzed, giving camphoroxalic acid. This difference in behavior is somewhat analogous with that found between formyl camphor and ethylic camphorcarboxylate,  $C_8H_{14}\left\langle\begin{array}{l} CH.CO,OC_2H_5 \\ | \\ CO \end{array}\right.$, to which reference has already been made. I have previously shown (*loc. cit.*) that ethylic camphoroxalate combines with phenylhydrazine, although the resulting monohydrazone or hydrazide,

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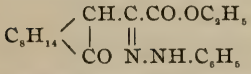
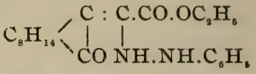
[1] Ann. Chem. (Liebig), 281, 319.

[2] *Loc. cit.*



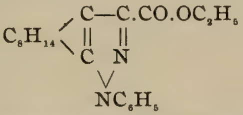
$$C_8H_{14}\left\langle\begin{array}{l} CH.C.CO.OC_2H_5 \\ |\quad\ \ \| \\ CO\ \ N.NH.C_6H_5 \end{array}\right.$$

or



$$C_8H_{14}\left\langle\begin{array}{l} C : C.CO.OC_2H_5 \\ |\quad\ \ | \\ CO\ \ NH.NH.C_6H_5 \end{array}\right.$$

was not obtained in a state of complete purity. This compound, under the conditions described below, loses the elements of water and forms ethylic camphylphenylpyrazolecarboxylate

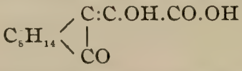


which, when hydrolyzed, yields the free acid.

Camphoroxalic acid, $C_{12}H_{16}O_4$, I had also prepared before. It is extremely stable towards alkali, and may be boiled for several hours with concentrated aqueous alcoholic potash or soda, without undergoing decomposition. With hydroxylamine, at the ordinary temperature, in presence of sodium hydrogen carbonate, it yields an additive compound,

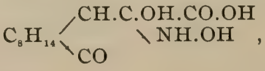
$$C_{12}H_{16}O_4.NH_3O.$$

The formation of this tells in favor of the formula



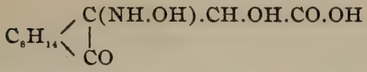
$$C_8H_{14}\left\langle\begin{array}{l} C:C.OH.CO.OH \\ | \\ CO \end{array}\right.$$

for the acid, since it is scarcely to be expected that hydroxylamine would yield a stable compound of such a nature with a substance containing two carbonyl groups. In accordance with this, the formula of the additive compound is



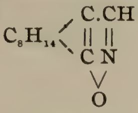
$$C_8H_{14}\left\langle\begin{array}{l} CH.C.OH.CO.OH \\ \qquad\quad \diagdown NH.OH \\ CO \end{array}\right. ,$$

the alternative formula



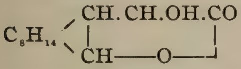
$$C_8H_{14}\left\langle\begin{array}{l}C(NH.OH).CH.OH.CO.OH\\ |\\ CO\end{array}\right.$$

being eliminated by the production of camphylisoxazole



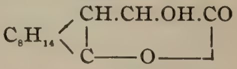
$$C_8H_{14}\left\langle\begin{array}{l}C.CH\\ \|\;\;\|\\ C\;\;N\\ \;\;\vee\\ \;\;O\end{array}\right.$$

which Bishop, Claisen, and Sinclair were unable to prepare from sodium formylcamphor and hydroxylamine hydrochloride (*loc. cit.*). The production of a γ-lactone



$$C_8H_{14}\left\langle\begin{array}{l}CH.CH.OH.CO\\ |\qquad\qquad\qquad |\\ CH—O—\!\!\lrcorner\end{array}\right.$$

(not

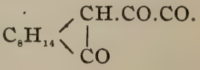


$$C_8H_{14}\left\langle\begin{array}{l}CH.CH.OH.CO\\ |\qquad\qquad\qquad |\\ C—O—\!\!\lrcorner\end{array}\right.$$

as given in my first paper) by the reduction of camphoroxalic acid, is equally compatible with either the keto- or hydroxy-formula.

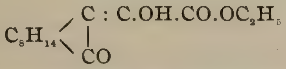
Experimental.

Preparation of Ethylic Camphoroxalate,



$$C_8H_{14}\left\langle\begin{array}{l}CH.CO.CO.OC_2H_5\\ |\\ CO\end{array}\right.$$

or



$$C_8H_{14}\left\langle\begin{array}{l}C:C.OH.CO.OC_2H_5\\ |\\ CO\end{array}\right.$$

.—The various methods of preparation described below were tried in order to determine the most favorable conditions for the formation of this compound.

I. *Sodium Wire and Ether.*—Camphor (21 grams = $1\frac{1}{8}$ molecule) was mixed with ethylic oxalate (14.6 gram = 1 molecule), and ether (200 cc.) purified by means of sodium, and sodium (2.3 gram = 1 atom) in the form of thin wire quickly added. A white flocculent precipitate is soon formed; this turns yellow in a few moments, and then dissolves; the ether usually boils vigorously, but cooling is scarcely necessary. When the reaction slackens the flask, attached to a reflux-condenser, is heated on the water-bath during 10–15 minutes, and then allowed to remain at the ordinary temperature for about twenty-four hours. A small quantity of the sodium salt usually remains undissolved. The ethereal solution is poured into ice-water, well shaken, and the ethereal layer removed. The aqueous solution is again extracted with ether, the latter being added to the first extract (Sol. *A*). More ether is added to the aqueous liquid, and then dilute ice-cold sulphuric acid in excess. After shaking, the ether is removed, and the residue extracted twice more with ether. The three ethereal solutions are combined, dried over calcium chloride, and distilled. The residue consists of crude ethylic camphoroxalate together with some ethylic oxalate. The aqueous residual liquid does not react with copper sulphate solution even in presence of ammonia. The ethereal solution *A* is dried, the ether removed, and the residue, consisting of camphor, borneol, and camphoroxalic acid is mixed with concentrated sodium hydrate solution in considerable excess, dilute alcohol being added so as to bring the whole into solution; the liquid is then boiled during 1–2 hours, the greater portion of the alcohol is distilled off, the residue mixed with water, filtered, and well washed. The whole of the borneol and camphor remain on the filter. The filtrate is treated with dilute sulphuric acid in excess, extracted three times with ether, and this, when dried and distilled, leaves the camphoroxalic acid, which, after crystallization once or twice from ligroïn of low boiling-point, is sufficiently pure for ordinary purposes. The yield of ester and purified acid is 58 per cent. of the theory.

II. *Sodium Wire and Ligroïn* (*Boiling-point 64-70°*).—The ligroïn is carefully dried over sodium wire. The experimental details are similar in every respect to the foregoing, but the borneol, etc., is removed by means of ligroïn, the extractions after acidification being made with ether. The materials were taken in the proportion given in the previous experiment except that 300 cc. ligroïn were employed. The yield of crude ethylic salt alone was 63.5 per cent. of the theoretical. The reaction appears to proceed somewhat more slowly than when ether is used, and the mixture requires heating for a rather longer period. Camphor (31.5 gram =

1.5 molecule), ethylic oxalate (21.9 gram = 1 molecule), sodium (3.5 gram = 1 atom), and ligroïn (500 cc.) gave a combined yield of ester and acid of 92.4 per cent. of the theoretical. Camphor (44.6 gram = 2 molecules), ethylic oxalate (21.8 gram = 1 molecule), sodium (6.9 gram = 2 atoms) and ligroïn (500 cc.) gave a combined yield of 66.5 per cent. of the theoretical. This experiment was made in order to test, as far as possible, whether the mechanism of the reaction accorded with the explanation given in the theoretical part, or whether the camphor and sodium first reacted according to the equation $2C_{10}H_{16}O + 2Na = C_{10}H_{15}ONa + C_{10}H_{17}ONa$. The sodium dissolved comparatively slowly, and the liquid required heating on the water-bath during about thirty-five minutes. The ethylic salt was darker than usual (see later).

III. *Sodium Ethylate and Ether.*—The sodium ethylate was made from Kahlbaum's absolute alcohol, dried in a current of purified hydrogen, powdered, and passed through a fine sieve. For the experiment it was suspended in ether that had been purified by means of sodium, the camphor and ethylic oxalate were added in equimolecular proportion, and, as no reaction occurred at the ordinary temperature, the mixture was boiled during eight hours with a reflux-apparatus. It gradually turned yellow, but the sodium salt did not dissolve to any great extent. The contents of the flask were poured into ice-water, acidified with dilute sulphuric acid, and worked up in the usual manner. The crude ethylic salt gave the ferric chloride reaction, but, when hydrolyzed in the manner described in the first paper, the yield of acid was only 10 per cent. of the theoretical. The method is therefore useless, as a means of preparation.

IV. *Sodium Ethylate in Alcoholic Solution.*—The sodium (1 atom) was dissolved in absolute alcohol in a reflux-apparatus, the camphor and ethylic oxalate added in equimolecular proportion, and the solution heated on the water-bath during 3–4 hours. Rather more than half of the alcohol was distilled off, the residue poured into ice-water, and treated as in the preceding experiment, except that the liquid was extracted four times with ether. The crude ethylic salt deposited crystals of camphor after some time. It was converted into the acid of which it yielded 4.4 per cent. of the theoretical. Like the preceding method, this is quite unsuited for the preparation of the compound. The following table gives a comparison of the results obtained, methods III and IV being omitted for the reason stated :

Experiment.	Menstruum.	Molecules camphor to 1 molecule ethylic oxalate.		Atoms sodium.	Crude ethylic salt and acid. Per cent. of theoretical.
1	Ether	$1\frac{1}{3}$	:	1	58.0
2	Ligroïn	$1\frac{1}{3}$	:	1	63.5[1]
3	"	$1\frac{1}{2}$	:	1	92.4
4	"	2	:	2	66.5

As compared with ether ligroïn is beneficial to the yield: it has the advantages of cheapness and facility of dehydration, hence it was always employed for the preparation of the ethylic camphoroxalate on a large scale. The ethylic salt obtained in experiment III was comparatively pure, as shown by its behavior towards phenylhydrazine. The relatively small yield in experiment IV is discussed in connection with camphoroxalic acid.

In ethereal or ligroïn solution ethylic camphoroxalate does not react with an aqueous solution of copper acetate ; with neutral solutions it yields, on evaporation, a soft crystalline residue, which smells of camphor. An ammoniacal solution of copper acetate, under similar conditions, gives a green varnish. A further attempt to prepare a copper salt was made as follows : the crude ethereal solution of sodium ethylic camphoroxalate, containing therefore borneol, etc., was acidified with acetic acid and copper acetate added. No copper salt was precipitated, and none was obtained on evaporation. Ethylic camphoroxalate thus presents a marked contrast with formylcamphor, which is a strong acid. The influence of various radicles on the power of forming copper salts which 1,3-diketones exhibit, has been investigated to some extent by Claisen and Ehrhardt ;[2] ethylic camphoroxalate most closely approaches ethylic ethylacetoacetate in this respect.

An attempt was made to purify ethylic camphoroxalate by distillation. After removal of traces of ether and alcohol, the temperature rose to 150°; the portion passing over at 180°–185° showed no definite boiling-point. A considerable carbonaceous residue was left in the flask, no sublimate (camphor) could be observed. The distillate gave the ferric chloride reaction. When again distilled (75 mm.) carbon dioxide was evolved at 103°; at 115° an oil passed over together with a crystalline substance, apparently camphor; it dissolved in the oil and, although separation took place at the temperature of a freezing-mixture, it redissolved too quickly to admit of removal. The distillate gave the ferric chloride reaction. From the residue in the flask, camphoroxalic acid was isolated in comparatively large amount. The distillate when further examined, proved to contain camphor, camphoroxalic acid, and an acid that rapidly reduced an ammoniacal solution of silver nitrate at the ordinary temperature. Oxalic acid could not be detected. The chief effect of heat on ethylic camphoroxalate is apparently to resolve it, no doubt by the agency of traces of water, which are unavoidably present, into alcohol and camphoroxalic acid, a little ethylic salt probably distils over; the remainder is then further decomposed into camphor and ethylic hydrogen oxalate which, at the temperature of the experiment, is resolved into carbon dioxide and ethylic formate. As the quantity of these substances was relatively small, it would appear as if the decomposition was chiefly confined to the ethylic salt. (Compare action of heat on camphoroxalic acid.)

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[1] Ethylic salt only.

[2] Ber. d. chem. Ges., **22**, 10.

It is known that ethylic malonate and ethylic oxalacetate can be separated from their alkyl derivatives by systematic treatment with solutions of sodium hydrate, sodium carbonate, and sodium hydrogen carbonate. The following experiments were therefore performed in the hope that in this manner the purification of ethylic camphoroxalate might be effected; at the same time the degree of its acidic properties, if any, would be exhibited. The ethylic salt was shaken with a solution of sodium hydrate (1 : 10) for a few moments, and the solution extracted with ether (Sol. *A*), which was then washed with dilute sulphuric acid. The aqueous residue was acidified with dilute sulphuric acid and extracted with ether

(Sol. *D*). This was washed successively with a solution of sodium carbonate (1 : 10) and a solution of sodium hydrogen carbonate (saturated). Both these solutions were then acidified and extracted with ether, giving solutions *B* and *C*, respectively. All the operations were performed as quickly as possible. The ethereal solutions, after being dried and the ether removed, gave residues as follows :

A. Greatest in amount ; consisted chiefly of camphoroxalic acid.

B. Very small quantity of oil giving ferric chloride reaction.

C. One drop of colorless oil ; no reaction with ferric chloride.

D. Two drops of slightly colored oil, giving ferric chloride reaction.

These results confirm the conclusions arrived at by a study of the behavior of ethylic camphoroxalate and copper acetate, and they show with what extreme readiness the ethylic salt is hydrolyzed ; although possibly the pure compound might prove more stable in this respect.

Phenylhydrazine and Ethylic Camphoraxalate.

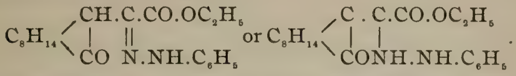
Ethylic camphoroxalate, in anhydrous ethereal solution, immediately reacts with phenylhydrazine (equimolecular proportions); the liquid becomes warm, and an oily solid is deposited; the mixture is boiled on the water-bath with a reflux-apparatus during four to five hours. The white, granular solid is separated by filtration, well washed with anhydrous ether, and recrystallized from a mixture of methylic alcohol and ether. It then appears homogeneous. When quickly heated it softens at 175°, and melts and evolves gas at 178°. Analyses showed that it is not quite pure. After recrystallization from the same solvent it is deposited in very slender, small, white needles, melting sharply at 212°. The yield is very good. Analysis gave the following results:

0.2043 gram substance gave 0.1374 gram H_2O, and 0.5220 gram CO_2.

0.1984 gram substance gave 13.8 cc. N_2 at 18.5° and 746.5 mm. = 744.1 mm. cor.

	Calculated for $C_{20}H_{26}N_2O_3$.	Found.
C	70.17	69.69
H	7.60	7.48
N	8.19	7.84

The compound is, therefore, the monophenylhydrazone or phenylhydrazide,



$$C_8H_{14}\left\langle\begin{array}{l}CH.C.CO.OC_2H_5\\ |\qquad \|\\ CO\ \ N.NH.C_6H_5\end{array}\right. \text{ or } C_8H_{14}\left\langle\begin{array}{l}C\ .\ C.CO.OC_2H_5\\ |\quad\ |\\ CONH.NH.C_6H_5\end{array}\right. .$$

It was briefly described in the previous paper (loc. cit.) but, as the low melting-point (187°–188°) shows, it was not completely purified. The compound gives a deep blue purple coloration with concentrated nitric acid, is readily soluble in alcohol, less so in methyl alcohol, sparingly in ether, and in toluene. It is comparatively stable towards sodium hydrate at the ordinary temperature. When boiled, a faint pink coloration is produced. With ferric chloride and alcohol no color is obtained. The ethereal mother-liquor and washings collected during the preparation of the compound leave, on distillation, a red oil, which contains ethylic oxalate derived from the crude ethylic camphoroxalate employed.

Preparation of Ethylic Camphylphenylpyrazolcarboxylate.

This substance is formed by heating the phenylhydrazone just described at about 200°, steam being evolved, but its separation from unchanged hydrazone and oily products is attended with difficulty, and the yield is rather poor. It can also be obtained by warming the phenylhydrazone with acetic anhydride and fused sodium acetate. The product of the reaction is dissolved in water and on neutralizing with sodium carbonate the pyrazol is precipitated. It is formed when the phenylhydrazone is dissolved in glacial acetic acid, a few drops of concentrated hydrochloric acid added and the solution warmed on the water-bath during forty-five minutes. The acid liquid is diluted, neutralized with sodium carbonate, and the pyrazol extracted by means of ether. It is also obtained by saturating at 0° a solution of the phenylhydrazone in glacial acetic acid, with dry hydrogen chloride. The liquid is allowed to remain at this temperature during one and one-half hours, poured into water, and the solution treated in the manner above described. The pyrazol is best prepared by suspending the finely divided phenylhydrazone, which need not have been recrystallized, in about half the quantity of absolute alcohol needed for its solution, and saturating the liquid at 0° with dry hydrogen chloride. The phenylhydrazone usually dissolves quickly, but occasionally a fugitive white flocculent precipitate is formed resembling aluminium hydroxide. The stream of gas is continued until a clear solution is obtained, and the liquid is then allowed to remain at 0° during one and one-half hours. The alcohol is distilled off on the water-bath, the residue washed with a solution of sodium carbonate, dried, and recrystallized from ether-ligroïn. The yield is practically quantitative. The compound crystallizes in bunches of white needles, melting at 116 ~~114~~°. It is readily soluble in alcohol, less so in ether, and sparingly in ligroïn. It gives a pale yellow colored solution with concentrated nitric acid; is precipitated unchanged from its alcoholic solution by the addition of a solution of ferric chloride; is insoluble in a boiling solution of sodium hydrate, in boiling dilute sulphuric acid, but readily dissolves in hot acetic acid. The analysis gave the following results:

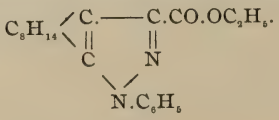
0.2758 gram substance gave 0.1847 gram H_2O and 0.7458 gram CO_2.

(1) 0.1557 gram substance gave 12 cc. N_2 at 18.5° and 744.5 mm. = 742 mm. (cor.).

(2) 0.2508 gram substance gave 19.2 cc. N_2 at 16° and 750.1 mm. = 748 mm. (cor.).

	Calculated for $C_{20}H_{24}N_2O_2$.		Found.
C	74.07		73.75
H	7.40		7.44
		(1)	(2)
N	8.64	8.66	8.78

The properties and mode of formation of the compound agree with the formula



$$C_8H_{14}\left\langle\begin{array}{c}C.\text{——}C.CO.OC_2H_5.\\ \| \qquad\quad \| \\ C \qquad\quad N \\ \diagdown \ \diagup \\ N.C_6H_5\end{array}\right.$$

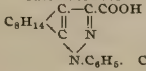
In the light of C. Walker's[1] investigation of the condensation-products of ethylic acetoacetate phenylhydrazide it is interesting to observe that ethylic camphoroxalate phenylhydrazone yields the same pyrazol both at high and at low temperatures.

Camphylphenylpyrazolcarboxylic Acid.

The preceding compound is readily hydrolyzed by dissolving it in the minimum quantity of alcohol, and adding potash (2 parts), dissolved in a little water. The solution is warmed on the water-bath during about thirty minutes until it becomes clear. It is then cooled, and acidified with dilute sulphuric acid. After remaining for a short time, the crystalline precipitate is removed, dried, and recrystallized twice from benzene, with or without the addition of ligroïn. The yield is quantitative. The crystals first formed consist of lustrous needles; they appear to contain some of the solvent as they slowly lose their lustre at the ordinary temperature, more quickly when warmed. The recently prepared crystals melt at 192°; after drying, at 197°. The acid is very sparingly soluble in water, and practically insoluble in ligroïn. It readily dissolves in benzene, and in hot toluene, but is less soluble in ether. Concentrated nitric acid gives no coloration; with alcohol and ferric chloride a brownish-red color is produced which becomes more red on heating. The compound has well marked acidic properties; it readily dissolves in a solution of sodium hydrate at the ordinary temperature, and in a solution of sodium carbonate on warming, carbon dioxide being liberated. From these solutions it is reprecipitated by acids. The analyses gave the following results:

0.3980 gram substance gave 29.2 cc. N_2 at 17.5° and 745.5 mm. = 743 mm. (cor).

0.2227 gram substance gave 19.6 cc. N_2 at 19° and 744 mm. = 741.5 mm. (cor).

	Calculated for  $C_8H_{14}\langle C.-C.COOH \,\|\, C = N \rangle N.C_6H_5$.	Calculated for $C_{18}H_{20}N_2O_2+\frac{1}{2}C_6H_6$.	Found. (1)	(2)
N	9.45	8.35	8.30	9.86

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[1] This JOURNAL, 14, 576.

The first analysis was made with air-dried material, the second with substance dried at 100°. The *salts* of the heavy metals are insoluble and amorphous. The copper salt is greenish-blue, the ferric salt buff, the lead and barium salts white.

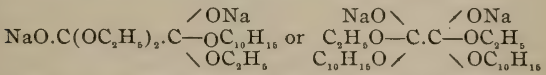
Camphoroxalic Acid.

In the previous paper (*loc. cit.*) the preparation of this compound from ethylic camphoroxalate was described, but subsequent experiments have shown that its stability is much greater than was formerly believed to be the case, and that it is needless to hydrolyze at the ordinary temperature. Its separation from the crude borneol residues was also detailed. It is found that the use of sodium ethylate for this purpose is not necessary ; sodium hydrate meets all requirements, as described above, in the preparation of the ethylic salt. An attempt was made to separate it from the borneol and camphor by distillation. The crude ligroïn-extract was dried, the ligroïn removed, and the residue fractionated; at 60°–100° a little ligroïn passed over, and the temperature then rose to 200°, at which point carbon dioxide was evolved, and a white sublimate formed. The contents of the flask did not boil at 220°. The sublimate melted at 192°–194°, and appeared to consist of camphor and borneol. The residue was freed from carbonaceous matter by sublimation, and melted at 180°–184°. It had a smell like that of camphor. The acid is insoluble in cold, but slightly soluble in hot, water. It crystallizes from ligroïn in hexagonal, not quadratic, plates, and the well-developed crystals resemble those of quartz in form. In a dilute solution of sodium hydrate it instantaneously decolorizes a solution of potassium permanganate. With lime water, or a solution of calcium chloride and ammonium hydrate, a white flocculent precipitate of the calcium salt is formed. This is readily soluble in acetic acid, and its production serves as a convenient test for the presence of the acid. The following table gives the yield of acid under varying conditions ; the numbers of the experiments refer to the previous table (which see):

	Ethylic oxalate—1 mol.				
Experiment.	Molecules camphor.		Atoms sodium.	Acid formed. Per cent. of theory.	Acid : 1 pt. of ester.
1	$1\frac{1}{3}$	:	1	4.9	0.07
3	$1\frac{1}{2}$	:	1	17.0	0.2
4	2	:	2	44.6	1.8

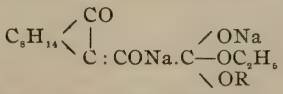
The production of the acid may be due to one or more of the following causes:

1. Traces of moisture in the apparatus employed. 2. Hydrolysis of the ethylic salt whilst the borneol is being extracted. 3. To the borneol and excess of camphor retaining ethylic salt which is afterwards hydrolyzed in subsequent operations (see above). 4. To hydrolysis by means of the sodium ethylate. No doubt some acid is produced by the first three causes, but as they were practically constant during all the experiments, they do not explain the gradual increase. As to the fourth possibility, whilst sodium ethylate readily hydrolyses fats and oils, there is no reason to suppose that it would act in this manner under the conditions mentioned. The proportion of acid formed is dependent apparently on that of camphor and sodium present, and, to some extent, on the duration of the heating. Its production appears to be analogous with that of acetophenoneoxalic acid described by Brömme and Claisen,[1] who explain the reaction by assuming the formation of the intermediate compound, $\mathrm{NaO.C(OC_2H_5)_2.C(OC_2H_5)_2.ONa}$. In the case of camphoroxalic acid the additive compound would be either



$$\mathrm{NaO.C(OC_2H_5)_2.C}\begin{array}{l}\diagup\mathrm{ONa}\\ -\mathrm{OC_{10}H_{15}}\\ \diagdown\mathrm{OC_2H_5}\end{array}\text{ or }\begin{array}{r}\mathrm{NaO}\diagdown\\ \mathrm{C_2H_5O}-\\ \mathrm{C_{10}H_{15}O}\diagup\end{array}\mathrm{C.C}\begin{array}{l}\diagup\mathrm{ONa}\\ -\mathrm{OC_2H_5}\\ \diagdown\mathrm{OC_{10}H_{16}}\end{array}$$

according to whether the ethylic oxalate combines with two molecules of sodium camphor, or with one of this and one of sodium ethylate. The ortho compound then reacts with more camphor in the manner already described giving



$$\mathrm{C_8H_{14}}\left\langle\begin{array}{l}\mathrm{CO}\\ \,|\\ \mathrm{C:CONa.C}\begin{array}{l}\diagup\mathrm{ONa}\\ -\mathrm{OC_2H_5}\\ \diagdown\mathrm{OR}\end{array}\end{array}\right.$$

which, when poured into water, yields

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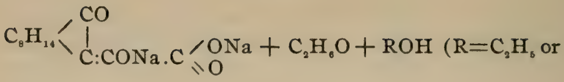
[1] Ber. d. chem. Ges., **21**, 1132.



$$C_8H_{14}\left\langle\begin{matrix}CO\\ |\\ C{:}CONa.C\left\langle\begin{matrix}ONa\\ O\end{matrix}\right.\end{matrix}\right. + C_2H_6O + ROH\ (R{=}C_2H_5\text{ or }C_{10}H_{15}).$$

This explanation also accounts for the necessary prolongation of the heating.

Camphoroxalic Acid and Hydroxylamine.

The acid (1 mol.) is dissolved in the smallest requisite amount of alcohol; an equal weight of hydroxylamine hydrochloride (3.5 mol.) is dissolved in the minimum quantity of water, the solutions mixed, more alcohol added, if necessary, then solid sodium hydrogen carbonate in excess. After remaining at the ordinary temperature during three to four days, the liquid, if sufficiently concentrated, becomes permeated with a mass of slender, colorless needles, consisting of a sodium salt. It is acidified with dilute sulphuric acid, extracted three times with ether, and the ethereal solution dried and distilled. The residue is purified by dissolving in ether, and adding ligroïn. It crystallizes in bushy clusters of colorless, lustrous needles, and in long narrow plates, and melts at 146.5° with evolution of gas. The yield is about equal to the weight of acid employed. The compound is readily soluble in water, methyl alcohol, and ether, almost insoluble in ligroïn and in dilute sulphuric acid. It is a comparatively strong acid and dissolves easily, at the ordinary temperature, in sodium carbonate, carbon dioxide being evolved, and also in a solution of sodium hydrate, and this, when boiled, does not evolve alkaline fumes. No coloration is produced with a solution of ferric chloride. Analysis shows that the substance is an additive compound.

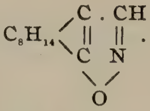
0.2224 gram substance gave 0.1500 gram H_2O and 0.4554 gram CO_2.

0.1705 gram substance gave 8.6 cc. N_2 at 21° and 739 mm. = 736.3 mm. (cor.).

	Calculated for $C_8H_{14}\left\langle\begin{matrix}CH.C.OH(NH.OH)CO.OH\\ |\\ CO\end{matrix}\right.$	Found.
C	56.03	55.85
H	7.40	7.49
N	5.44	5.55

The copper and lead salts are apparently amorphous; the former is pale blue, the latter white; both are formed only in ammoniacal solution.

Camphylisoxazole,



The preceding compound (1 part) is dissolved in a mixture, consisting of glacial acetic acid (2 parts) and acetic anhydride (1 part), and the solution heated for a few minutes on the water-bath until the color darkens. It is then poured into water, neutralized with sodium carbonate, and extracted three times with ether. The ethereal solution is dried, the ether distilled, and the residue purified by solution in glacial acetic acid. On the addition of water, colorless lustrous needles are formed, melting at 124°–125°. The compound slowly sublimes at about 70° and is deposited in clusters of very slender, silky, lustrous needles. It is readily soluble in glacial acetic acid, ether, toluene, and alcohol; almost insoluble in ligroïn. It instantly dissolves in concentrated nitric acid, but gives no coloration with it or with ferric chloride and alcohol. It dissolves in water, and in a solution of sodium carbonate when boiled, and in a solution of sodium hydrate on warming, but is reprecipitated from all three by cooling. The analyses gave the following results:

(1) 0.2257 gram substance gave 0.1697 gram H_2O and 0.6122 gram CO_2.

(2) 0.2238 gram substance gave 0.1693 gram H_2O and 0.6058 gram CO_2.

0.1637 gram substance gave 11.4 cc. N_2 at 16° and 745.1 mm. = 743 mm. (cor.).

	Calculated for $C_{11}H_{15}NO$.	Found.	
		(1)	(2)
C	74.57	73.97	73.82
H	8.47	8.35	8.40
N	7.91	7.93	....

I should like to take this opportunity of expressing my thanks and obligations to Prof. Edgar F. Smith for his kindness in allowing this work to be continued in the John Harrison Laboratory.

UNIVERSITY OF PENNSYLVANIA,
PHILADELPHIA, PA.

Contribution from the Laboratory of General Chemistry, University of Michigan.

THE PREPARATION OF ZINC ETHYL.

By ARTHUR LACHMAN.

Of all the methods heretofore proposed for the preparation of zinc alkyls, the Gladstone-Tribe copper-zinc couple[1] gives by far the best results. As originally given, however, the directions are open to two practical objections. First of all, it is not always an easy matter to secure the zinc filings of necessary fineness. And secondly, while the careful fusion of the filings with the reduced copper offers no difficulties when carried out with 10-gram lots, as usually taken by the authors, it is practically impossible to prevent larger quantities from melting completely and forming a worthless solid ingot on cooling.

A form of zinc available in every laboratory is zinc dust. On removing the coating of oxide by heating in hydrogen for a short while, it was found that 50 grams each of the metal and ethyl iodide reacted within ninety minutes, and gave 14 grams of zinc ethyl (72 per cent. of the theoretical yield). When this metal is coupled with copper, by reducing an intimate mixture of zinc dust and finely powdered copper oxide, the time of reaction is shortened to thirty minutes, and the yield increased to nearly 90 per cent. Different varieties of zinc dust give different yields (ranging from 70 per cent. upward); this probably finds its explanation in the phenomena discussed by H. Wislicenus.[2] The actual quantities of materials taken also exercise an influence, the yield being somewhat smaller with larger quantities (100 grams or more). I have not attempted to ascertain the cause of this.

The details of the process are extremely simple. Zinc dust and copper oxide are mixed in the ratio of 100 to 12, loosely filled into a combustion-tube, and a current of hydrogen passed over the heated mixture for about twenty minutes. In order to prevent the condensation of moisture in the tube, with the consequent caking of the mass, it is best to heat the tube along its whole length at once. A dull red heat seems to give the best results; the nearer the melting-point of zinc the better, I presume. If the temperature be kept too low, the metals do not alloy well, and the results approach those given by zinc dust alone. I have usually employed equal quantities of ethyl iodide and metal couple, sometimes less metal; perhaps the yield might be increased by excess thereof. For further directions the article of Gladstone and Tribe had best be consulted. In place of the oil-bath for heating the zinc ethiodide, the Babo air-baths may be substituted, as being cleaner and more expeditious; if a small flame be placed under them at first, there is no danger of breaking the flask. By employing two sets of apparatus, and working up about 100 grams at a time, the process may easily be made continuous, and several hundred grams of zinc ethyl prepared in a single day. Mr. F. M. Tschirner, who has manufactured nearly 300 grams for me, found no difficulty in obtaining 150 grams in an afternoon.

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[1] J. Chem. Soc., 1879, 570.

[2] J. prakt. Chem. (2), **54**, 18 ff.

It is customary to preserve zinc ethyl in sealed tubes. This is awkward where small and varying quantities are frequently needed. Small Erlenmeyer flasks, with perfectly straight sides beginning at the very mouth, greatly facilitate the operation of pouring out the liquid, and when well corked form perfectly safe receptacles. Instead of requiring an assistant to keep a stream of carbon dioxide upon the mouth of the flask when transferring zinc ethyl, it is much more convenient to conduct all such manipulations under a small, inverted funnel, through which the gas is rapidly passing.

It had been my intention to compare the above described modification of the copper-zinc couple with the original, chiefly with respect to its reducing powers, but the recent article of H. Wislicenus[1] has made this unnecessary. Qualitive tests show that the new form reacts in much the same manner with alkyl and alkylene haloids as the older. I have attempted to use ethyl bromide in place of the expensive iodide, but without encouraging results. Methyl iodide reacts as readily as the ethyl compound, though the yield of zinc methyl was not determined.

ANN ARBOR, Dec., 1896.

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[1] *Loc. cit.*

A SIMPLE TEST FOR THE HALOGENS IN ORGANIC HALIDES.

By J. H. Kastle and W. A. Beatty.

In connection with some work on the displacement of bromine and iodine from their organic compounds, we had frequent occasion to test for the halogens in their organic derivatives, and, while a great many methods for conducting such tests were to be found in the literature, few, if any of these, could be conducted rapidly; and many involved the use of rather large amounts of substances, such as lime, soda-lime, etc., which are not readily obtained free from chlorine. It is unnecessary in this connection to enumerate the many tests which have been proposed for these elements in their organic compounds; most of them are already familiar to chemists, and nearly all of them are described in Beilstein's *Handbuch* and in Allen's *Commercial Organic Analysis*.

Appreciating the need therefore of a simpler and rapid test whereby chlorine, bromine and iodine could be recognized with certainty in their most stable and volatile organic combinations, it occurred to one of us (Kastle) to heat such compounds with a mixture of silver and copper nitrates, thereby oxidizing the organic matter and holding back any halogen present by means of silver. On experiment it was found that excellent results could be obtained with this mixture, which can always be obtained free from any traces of chlorine, bromine or iodine, by dissolving the metals in pure nitric acid and evaporating to crystallization. In the case of non-volatile substances the test is most easily conducted as follows: A small quantity of a substance to be tested, usually about 0.1 gram, is placed in the test-tube, along with about 0.5 gram of the mixed nitrates and a few drops of water. The tube is then gradually heated in the flame of the Bunsen burner until the nitrates are completely decomposed; the temperature never being allowed to rise higher than low red heat. The tube, in which some reduced copper is often seen, is allowed to cool, a little water and dilute sulphuric acid poured on the contents of the tube and a few pieces of metallic zinc added. After five or ten minutes, during which time any halogen compound of silver is reduced, the contents of the tube are filtered and a solution of silver nitrate added to the filtrate, together with a little dilute nitric acid, when the chloride, bromide or iodide of silver will be precititated, if either of these halogens was present in the substance tested.

Excellent tests for chlorine, bromine and iodine were obtained in this way in the following substances: Dibromnaphthalene, eosine, benzene dichlorsulphonamide, *p*-brombenzenesulphonamide, tribromphenol, potassium *p*-brombenzenesulphonate, monobromacetanilide, sozoiodol (Merck), barium *p*-iodobenzenesulphonate. With very volatile substances such as chloroform, it was found necessary to conduct the test in a tube about six inches long by one-quarter inch internal diameter, closed at one end, and bent twice at right angles at equal distances along the tube, so as to form a tube having somewhat the shape of the letter S. In making the test about $\frac{1}{4}$ cc. of the volatile compound to be tested was introduced into the closed end of the tube, and the tube so clamped as to give its open end an upward slant. About 0.5 gram of the dry mixed nitrates was then placed in the bend of the tube farthest removed from the closed end; after which the parts of the tube containing the substance to be tested and the nitrates were heated alternately, the former portion very gently, so as not to drive out the volatile substance before it could be oxidized by the decomposing nitrates. The heating is continued until all the nitrates are decomposed, and all of the substance to be treated volatilized, at the end of which time the tube is broken and the fragments, containing the oxides of copper and silver, placed in a test-tube with a small quantity of water and sulphuric acid and a few small pieces of zinc. The test is then completed in the manner described in the above. The following substances were tested in the closed S-shaped tubes with excellent results in every case:

Chloroform, isopropyl bromide, butyl bromide, ethyl chlorcarbonate, propyl bromide, propyl iodide, bromoform, ethylidene chloride, propyl chloride, monobrombenzene, dibrombenzene, ethylene bromide, monochloracetic acid, benzoyl chloride, dibromsuccinic acid.

It is believed that this test as applied both to volatile and to non-volatile organic halides has in it many points of advantage over those which have been proposed for this purpose; in the first place the test is rapid and certain in its result, and by means of it we can judge not only of the presence or absence of the halogens, but it can also be determined at a glance whether it is chlorine, bromine or iodine that is present in the organic compound. Secondly, only very small quantities of substances are required to make the tests, and the few simple reagents needed may be obtained free from any traces of halogen without the least difficulty.

STATE COLLEGE OF KENTUCKY,
FEBRUARY, 1897.

REVIEWS.

COMMERCIAL ORGANIC ANALYSIS: A treatise on the properties, proximate analytical examination, and modes of assaying the various organic chemicals and products employed in the arts, manufactures, medicine, etc.; with concise methods for the detection and determination of their impurities, adulterations, and products of decomposition. By ALFRED H. ALLEN, F.I.C., F.C.S. Second Edition. Revised and enlarged. Vol. III. Part III. Philadelphia: P. Blakiston, Son & Co. 1896.

In the preface to the last previously issued portion of this valuable work (in 1892), it was announced that Part III of Volume III would cover the whole of the then remaining ground, and complete the work. But the author has decided to reserve the subject of Proteids and Albuminoid Compounds for still another part, and has included in that recently published the alkaloids not already disposed of, the glucosides, unclassified vegetable bitter principles, the animal bases and acids, and cyanogen with its derivatives. These subjects are treated with the same care, clearness and comprehensiveness which have given character to the earlier portions of the work.

There is much of interest for the physiological chemist and medical man, and the chapter on the ptomaines is valuable from a medico-legal point of view, while the recent great extension in the use of the cyanide process for the extraction of gold gives commercial importance to the discussion of cyanide liquors, the assay of residues from electroplating and gilding, and from gold extraction, etc.

It is particularly satisfactory to find, along with careful consideration given to the work of others, so much evidence of individual laboratory experience on the part of the author himself. Mr. Allen's book deserves its well established place as one of the standard classics of the working chemical library.

J. W. MALLET.

ENGINEERING CHEMISTRY: A Manual of Quantitative Chemical Analysis, for the Use of Students, Chemists and Engineers. By THOMAS B. STILLMAN, M.SC., PH.D., Professor of Analytical Chemistry in the Stevens Institute of Technology. Easton, Pa.: Chemical Publishing Co. 1897.

It is not very easy fairly to judge this work. Its scope and intention are not clearly indicated by its title or by its table of contents. It is certainly not a general manual of quantitative chemical analysis; yet it begins with some exercises evidently intended for elementary study in this field, such as the "determination of sulphur trioxide in crystallized magnesium sulphate," and the "determination of chromium trioxide in potassium bichromate." On the other hand, if it be taken as a special treatise on chemical analysis applied to the purposes of the engineer, one sees with some surprise in the body of the work a discussion of the "determination of sulphuric acid and free sulphur trioxide in fuming Nordhausen oil of vitriol," (introduced immediately after the "determination of aluminum in iron and steel," and immediately before the "determination of manganese in iron and steel"); and of "sodium cyanide as a component of potassium cyanide," (just before the "chemical and physical examination of Portland cement"); chapters on "the chemical and physical examination of paper," and on "soap analysis,"—subjects but distantly related to engineering—and on "practical photometry" and "the electrical units," which are not chemical subjects at all.

While some of these matters appear rather out of place, there are others which, it would seem, might well have been included, but are not, as, for instance, the examination of ordinary lime and lime mortar, of stucco (plaster of Paris), and of explosive agents.

A good many small errors, and an occasional careless use of language, strike the eye of the reader, and produce an uneasy feeling that there may possibly be other and more serious defects of this kind amid the numerous facts and figures in the five hundred pages of the book. For example, on page 58, "Charlestown, S. C.;" on page 81, "Glosway" (for Ilosway or Ilosvay); at same place, "a solution of α-amidonaphthalene acetate," it is directed, is to be made thus, "two-tenths gram of naphthylamine is boiled with forty cc. of water," (no mention of acetic acid, which is moreover especially recommended by Ilosvay), "filtered and diluted to 400 cc." It would have been well to note that the solution he has recommended will not keep unaltered. On page 94 we note "The middle portion of the scale" (boiler scale) "was a mixture of carbon dioxide and the hydrated oxides"; on page 303, "Saara*n*" (for Saara*u*); on page 319, "Guthrie's" ("Gutrie's" in table of contents), "e*n*tectic" (for e*u*tectic) "alloys"; and on page 488, in the table of atomic weights of the principal elements, oxygen being taken = 16, the values given for the following elements are, "aluminum 27.5," "antimony 120.0," "barium 137.0," "tin 118.0," "uranium 240.0," "wolfram (tungsten) 184.0," and "zinc 65.0."

In connection with the methods for determining the individual constituents of substances examined, the *reasons* for making such determinations, and the practical use to be made of the results, are given in an irregular way, and with very different degrees of fulness and clearness.

There is undoubtedly much valuable matter in the book, but it cannot be said that it is well arranged, or digested with the precision and clear perspective in the exposition of general principles and minute details that makes a work of standard and permanent value. J. W. MALLET.

PTOMAÏNS, LEUCOMAÏNS, TOXINS AND ANTITOXINS. BY VICTOR C. VAUGHAN, PH.D., M.D., AND FREDERICK G. NOVY, SC.D., M. D. Third edition, revised and enlarged. Lea Brothers & Co. pp. 604.

The investigation of the chemical factors involved in disease, and the study of the chemistry of bacteria and cells in general, have received increased attention during recent years. The results thus far obtained have been incomplete. and unsatisfactory in many ways, and it has been a difficult task to compile and classify the data at hand. The third edition of Vaughan and Novy's Ptomaïns and Leucomaïns is a worthy successor to the two that have preceded it. The new volume has been carefully revised, and over 200 pages been added to the former contents. Among the material presented for the first time is a brief chapter on the examination of poisonous foods; the germicidal constituents of the blood are discussed with particular reference to recent work on the nucleins, and the problems of immunity and serum-therapy are treated in the light of the newer investigations. Referring to the more purely chemical portions of the book, practically all the important contributions of the last six years have been included. Thus, new material has been added to the description of muscarin and the members of the cholin group (p. 383). In the chapter on the chemistry of the leucomaïns the discussion of the basic constituents of the cell has been adapted to the results of the recent investigations of Kossel, E. Fischer, Drechsel, Krüger, Balke, etc. In this connection the detailed description of the chief methods for the separation of the alloxuric bodies (p. 475 ff.) is a valuable feature, as well as the consideration of the constitution of these compounds (p. 481). The work of Vaughan and Novy cannot fail to create a favorable impression; the treatment of the subject matter, though mainly historical, shows no lack of critical features (cf. p. 321), while new problems are suggested at every step. In a few instances there is revealed an obvious lack of proportions, as for example, in the chapter on foods containing poisons—of the entire eighty-one pages, no less than twenty-four are devoted to tyrotoxicon, a ptomaïn of undetermined composition isolated by Vaughan from poisonous cheese. The newer scientific nomenclature has been adopted for the most part, and the terms chemic, physiologic, chlorid, etc., replace the more familiar spelling. There are remarkably few errors, typographical or other. On p. 384, the structural formula for cholin is incorrectly printed. A complete and well arranged bibliography concludes a volume that forms a welcome and thoroughly valuable addition to current physiologico-chemical literature.

LAFAYETTE B. WENDEL.

A LABORATORY MANUAL OF INORGANIC CHEMISTRY. By RUFUS P. WILLIAMS. In charge of the Chemical Department of the English High School, Boston, etc. Boston: Ginn & Co. 1896.

This little book gives quite minute directions for the performance of one hundred experiments or laboratory exercises. It is intended to accompany some text-book and is evidently provided for a rather young set of pupils, the desire apparently being to have all the members of the class engaged at the same work at one time. This may frequently be necessary on account of a too small teaching staff, or for the convenience of the instructor; it is as frequently a disadvantage to the pupil. For if one thing seems evident in laboratory instruction, it is that the time required by different students for the performance of the same task is rarely the same. With the adoption of the drill system of experimentation the opportunity for the development of anything but a perfunctory method of work, would seem to be shut out.

It is hard to decide by a study of the experiments alone what the pupil will learn from their performance in connection with the study of a text-book. In response apparently to a demand which seems as wide-spread as it is inexplicable, the author plunges the student with far too little preparation into the labyrinth of qualitative analysis and "separations."

While the book by no means merits praise as if it were an ideal laboratory guide, it must be said it is quite full in its description of individual experiments and clear: of its kind it seems to be good—a kind, however, which too often teaches, "The science of chemistry consists in the memorizing of formulas and the balancing of equations." W. W. R.

LABORATORY CALCULATIONS AND SPECIFIC GRAVITY TABLES. BY JOHN S. ADRIANCE, A.M. Third edition, revised and enlarged. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1897. 144 pp. Price, $1.25.

This book is interleaved with blank pages and contains a collection of tables from various sources, including those for comparison of different systems of weights and measures, preparation of reagents, specific gravity and composition of a number of solutions, calculations of analytical results, and other odds and ends. The author states in the preface that his aim has been to offer to the student, as well as to the analytical chemist, a substitute for much of his laborious calculations. The arrangement in some of the tables is not systematic and no explanations are given as to their use, so that one who has had no previous experience in the use of such tables would perhaps find difficulty in interpreting them. In the tables for the conversion of $BaSO_4$ to S, $Mg_2P_2O_7$ to P_2O_5, and P_2, and some others, the calculations are made only to the second decimal, so that differences of less than ten milligrams cannot be determined by their use. As all determinations are accurate at least to the milligram, the additional calculations would have to be made and while the tables were being examined and the extra calculation made, the whole could be determined by use of the factor or by other simple methods. Although the book contains some tables which are of use in special cases, it cannot be recommended as suitable for general use, as intended by the author. J. E. G.

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AMERICAN

CHEMICAL JOURNAL.

Contributions from the Chemical Laboratory of the Case School of Applied Science.

XXVI.—THE CONSTITUENTS OF PENNSYLVANIA, OHIO, AND CANADIAN PETROLEUM BETWEEN 150° AND 220°.[1]

By Charles F. Mabery.

The conflicting statements published long ago, and still uncorrected, concerning the composition of the portions of Pennsylvania petroleum distilling at 150°, the absence of any information relating to the constituents of Ohio and Canadian petroleum, and the erroneous assumptions as to the composition of American petroleum based on the results of Markownikoff and his assistants in the Russian oil, taken together, render a study of these portions of American petroleum of extreme interest. One cannot fail to be impressed with the marked differences of opinion that have prevailed as to the composition of the portions of American petroleum with higher boiling-points. Some authorities, influenced by the profound investigations of the Russian chemists on the Caucasus oil, have believed that the constituents of American oil above 150° are naphtenes, with a reservation as to whether the series C_nH_{2n}, announced by Warren, should be accepted as naphtenes. Others, depending on the results of Pelouze and Cahours, which form the basis of the statements in chemical literature concerning the constituents of Pennsylvania petroleum, have held that the series $C_n H_{2n+2}$ does not find its last representative in nonane (boiling-point 151°). Similar differences of opinion have been expressed by practical oil men, those who have witnessed the development of the petroleum industry from the beginning, concerning the composition of these oils. Some believe that Canadian and Ohio oils are esentially and fundamentally different from the Pennsylvania oil. Others hold that the chief constituents are identical, and that differences observed in refining are due to variations in the proportions of the principal constituents, and to the presence in certain oils of small amounts of other bodies that are not found in all. I must admit that my earlier impressions on this subject have not been verified in the light of the results which will be presented. This work was undertaken with the expectation that Pennsylvania oil would prove to consist in its higher portions of a series $C_n H_{2n}$, and it is only after a great amount of laborious study, and a vast accumulation of analytical data, presenting unquestionable evidence that, for the hydrocarbons distilling within these limits of temperature, except those collecting at 196° and 216° from Canadian petroleum, this series must be discarded—that I accept this conclusion. Concerning the composition of Ohio and Canadian petroleum, in the beginning of this work, I had no preconceived ideas.

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[1] Presented to the American Academy of Arts and Sciences, October, 1896. Aid in the work described in this paper was given by the Academy from the C. M. Warren Fund for Original Research.

The separation of constituents with higher boiling-points presents greater difficulties than of those in the portions distilling below 150°. In the lower portions there is no danger of decomposition during distillation, both on account of greater stability of the hydrocarbons and because the unstable bodies, such as the nitrogen, oxygen, and sulphur compounds, as well as the more complex hydrocarbons, distil for the most part at higher temperatures. Then distillation in air has little if any effect on the lower constituents, while the portions distilling at higher temperatures cannot be volatilized in the presence of air without more or less decomposition. As has been shown, distillation *in vacuo* prevents changes due to inherent instability, and it excludes air, but it increases very much the labor of the separations. It has been found to be especially serviceable in separating the hydrocarbons under consideration, since these bodies are contained for the most part in portions of the first distillate boiling above the limits of cracking, and are consequently contaminated by the products of decomposition when distilled in air, and the decomposition-products are difficult to remove. Evidently any experiments on a laboratory scale may fail to reveal the presence of bodies that are present in proportionately minute quantities. It would be interesting, and from a commercial point of view doubtless profitable, to establish a more extended investigation involving the manipulation of at least a hundred barrels of crude oil, continuing the fractional separations of all portions until the individual hydrocarbons were as perfectly isolated as is done with smaller quantities in the laboratory. Such an investigation could only be undertaken at large expense, and a long time would be required to reach desirable results.

In undertaking this subject, the course to be followed was plain. There is but one method for the separation of these hydrocarbons, and it yields satisfactory results only after long and tedious application. Concerning the question as to whether fractional distillation can be relied on for the separation of hydrocarbons with boiling-points not far removed, it can, I think, be stated with confidence that distillations many times repeated under constant conditions may be expected to yield products whose composition can be determined, after suitable purification, as accurately as the methods of analysis will permit. But hydrocarbons separated from petroleum in this manner, before purification, may be contaminated by other bodies whose boiling-points are nearly the same. As an illustration, to ascertain whether Ohio petroleum contains a hydrocarbon boiling at 162°, a course of fractional separations under 730 mm. was repeated fifty times, forty-five times within one degree. One portion after treatment with fuming sulphuric acid had its specific gravity changed from 0.7717 to 0.7535, but it still distilled within the same limits. Another portion of the same distillate, after treatment with common concentrated sulphuric acid, gave a product with the same specific gravity and the same boiling-point as the oil before treatment. The crude distillate contained a certain amount of mesitylene (boiling-point 163°) sufficient, as will appear later, to affect seriously the percentages of carbon and hydrogen. In the main, the hydrocarbons described in this paper as collecting between 160° and 216° have the same boiling-points as those described by Warren, except one which collected at 162°. It is peculiar that these bodies have nearly the same boiling-points as the naphtenes separated by Markownikoff from the Russian oil. In previous investigations on these hydrocarbons, except those of Warren, evidently the course of distillation was not sufficiently extended to separate with any degree of purity the individual constituents. In the light of Warren's distillations and those here presented, it is evident that Pelouze and Cahours could not have carried their separations far enough to obtain individual products. Concerning the thoroughness of Warren's separations there can be no question. But the deficiency in his work on the hydrocarbons now under consideration was the result of the limited knowledge then prevailing concerning the general composition of petroleum. The aromatic hydrocarbons, the oxygen compounds, and the nitrogen compounds, were not then recognized, or were merely suspected as constituents of petroleum. In the purification of his distillates, the single method adopted by Warren consisted in boiling with sodium, as shown by the following statement: "I must state, however, once for all, that, unless specially mentioned, no one of the bodies operated upon had received any chemical treatment except that of boiling with sodium."[1] But that Warren suspected the presence in his distillate of other bodies is indicated by a quotation from one of his private papers, already mentioned in another paper: "The samples analyzed may have contained traces of more highly carbonized substances, and that it would be worth while to treat with $HOSO_3$, and $HONO_5$, and remove these."[2] It is evidently an error to consider the hydrocarbons $C_n H_{2n+2}$, especially the lower members, as unstable toward reagents. It has been our experience, in removing aromatic hydrocarbons from the distillate 160°–216°, that the principal constituents are not affected in the cold by a mixture of nitric and sulphuric acids, nor by fuming sulphuric acid even on warming. After purification, the boiling-points do not change in a long course of distillations. No doubt the stability diminishes with a rise in boiling-points, but it is sufficient to permit of purification of the members below 216°. All analyses in this paper point to the general composition $C_n H_{2n+2}$, except for the Canadian hydrocarbons 196° and 216°. If continued distillation or treatment with the means of purification we have adopted produces decomposition, the product should scarcely consist at least entirely of lower members of the same series.

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[1] Proc. Amer. Acad., **27**, 66.

[2] This JOURNAL, **17**, 745.

In the comparative examination, the results of which will be described in this paper, two principal objects were kept in view: one of chief importance, to determine the series of hydrocarbons which form the main body of American petroleum, and the other naturally following, to ascertain whether the composition of Pennsylvania, Ohio, and Canadian oils as regards their principal constituents is the same.

In undertaking a study of the portions of petroleum within the limits of temperature mentioned above, it was at first determined to prepare all distillates from the crude oils, and this has been done in part in the Ohio and Canadian oils. But when it was found that cracking in refining did not begin to any considerable extent below 225°, and that distillates from the refinery resembled in all respects, at least in their principal constituents, those obtained in vacuum-distillation, refinery distillates were more freely employed, especially from Pennsylvania oil. But most of the results on Ohio and Canadian oils were obtained in vacuum-distillates, the preparation of which was described in a former paper.[1] Further assurance against decomposition in the Pennsylvania product was gained by selecting during the "run" in the refinery distillation just that portion of the distillates that corresponds in gravity to the constituents desired. Experience showed that heavier portions of the crude distillate should be selected than those corresponding to the constituents required, since the boiling-points invariably decline many degrees in subsequent distillations.

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[1] Proc. Amer. Acad., **31**, 1; This JOURNAL, **17**, 713.

The refinery distillate employed was taken at 48°–50° Baumé, having a specific gravity of 0.7892 at 20°. It was very nearly colorless and gave no odor of decomposition. Forty-five liters of this distillate was fractioned within limits of 10°, 5°, 2°, and for a long time within 1°. It gradually collected in heaps, as described by Warren, but the prolonged distillation was necessary to separate higher and lower constituents from the mixtures between.

Concerning the impression that Pennsylvania petroleum has the same composition between these limits as the Russian oil, which is based in part on the results of Warren suggesting the series $C_n H_{2n}$, and in part on the erroneous statements of Höfer, that Markownikoff found the same series in Pennsylvania that he had reported in Russian oil, it may be stated once for all that this identity is clearly excluded by the great difference in specific gravity of the corresponding distillates, without reference to the differences in percentage composition. These differences in composition are indicated at the outset by great differences in specific gravity of crude distillates at 16°, as shown by Markownikoff and Oglobine.[1]

Baku.		American.
150°–200°	0.786	0.757
200°–250°	0.824	0.788
250°–320°	0.681	0.809

The same differences appear between the individual constituents:[2]

Baku naphtenes		B. P.	Specific gravity.
Dekanaphtene	$C_{10}H_{20}$	160°–162°	0.795 (0°)
Endekanaphtene	$C_{11}H_{22}$	180°–185°	0.8119 (0°)
Dodekanaphtene	$C_{12}H_{24}$	196°–197°	0.8055 (14°)

—and the series $C_n H_{2n}$ of Warren, purified only by distillation and boiling with sodium:[3]

		B. P.	Specific gravity at 0°.
Rutylene	$C_{10}H_{20}$	174°.9	0.7703
Margarylene	$C_{11}H_{22}$	195°.8	0.7822
Laurylene	$C_{12}H_{24}$	216°.2	0.7905

As will be shown later, the specific gravity assigned by Warren to these constituents is very materially diminished by the removal of the aromatic hydrocarbons, and perhaps of other heavier bodies, that can only be separated by the application of more vigorous means of purification than Warren applied.

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[1] Ber. d. chem. Ges., **16**, 1873.

[2] *Ibid.*, 1877.

[3] Proc. Amer. Acad., **27**, 15.

Decane, $C_{10}H_{22}$, 163°–164°.

When Pelouze and Cahours announced that the hydrocarbon $C_{10}H_{22}$ is a constituent of Pennsylvania petroleum boiling at 160° ("sensiblement"), the presence in petroleum of the aromatic hydrocarbons had not been demonstrated, and since treatment with concentrated sulphuric acid and carbonate of soda was the sole means of purification, it is evident that their product must have still contained mesitylene (boiling-point 163°), which, according to Engler, is contained in petroleum to the extent of 0.2 per cent. Then the specific gravity, 0.757 at 15°, assigned by them, is somewhat higher than that of this decane with mesitylene entirely removed. Warren did not observe the collection of a distillate at this point in any considerable quantity. But if, as it seems probable, Pelouze and Cahours investigated, not Pennsylvania, but Canadian petroleum, the close agreement between their specific gravity of decane at 160° with ours in Canadian petroleum is explained. In attempting to ascertain whether a hydrocarbon with this boiling-point is present in Pennsylvania petroleum in any considerable amount, the distillates 150°–170° were carried through a long series of distillations, until several hundred grams collected between 158° and 162° under 730 mm., and finally more than 100 grams between 162° and 163° under 760 mm. One portion of this distillate was dried over sodium for analysis.

0.1453 gram of the oil gave 0.4560 gram CO_2, and 0.1865 gram H_2O.

	Calculated for		
	$C_{10}H_{22}$.	$C_{10}H_{20}$.	Found.
C	84.51	85.71	85.58
H	14.49	14.29	14.27

A determination of the specific gravity of this oil at 20° gave 0.7684. Its vapor-density was determined by the Hofmann method in the vapor of aniline.

0.1327 gram of the oil gave 66.8 cc. of vapor at 182°, under a tension of 373.2 mm.

II. 0.1113 gram of the oil gave 59.5 cc. of vapor at 182°, under a tension of 354.7 mm.

Calculated for $C_{10}H_{22}$.	Found. I.	II.
4.92	5.21	5.16

A portion of the same distillate was treated with fuming sulphuric acid with the aid of heat, and occasional agitation. When first added, a slight rise in temperature was observed, doubtless caused by the formation of mesitylenesulphonic acid. The acid was diluted, neutralized with baric carbonate, and the filtered solution evaporated nearly to dryness. A barium salt separated in clusters of needles, sparingly soluble in cold, more so in hot water. The quantity of this salt was too small for analysis. Another portion of the same distillate with a mixture of nitric and sulphuric acids in the cold formed an oily layer above the acids, which became solid on standing, and after crystallization from hot alcohol the needles that separated melted at 83°–84°, the melting-point of dinitromesitylene being 86°. When the dinitro product was warmed with fuming nitric acid, it formed prisms sparingly soluble in alcohol, and melting at 225° (melting-point of trinitromesitylene, 230°). In the treatment with acids, 16 grams of the crude distillate gave 8 grams of the purified oil, with a loss of 50 per cent. When treated with fuming sulphuric acid, 16 grams of the crude product gave 9.5 grams of the pure oil, with a loss of 40 per cent. Mesitylene formed, therefore, a considerable proportion of the crude distillate. The purified oil had the faint odor characteristic of pure petroleum hydrocarbons. After the removal of the hygroscopic moisture, the oil had no effect on bright metallic sodium. It gave upon analysis values required for decane :

0.1644 gram of the oil gave 0.5084 gram CO_2, and 0.2284 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.34
H	15.49	15.44

The specific gravity of the purified oil at 20° was 0.7479, a value somewhat lower, as mentioned above, than that formed by Pelouze and Cahours.[1]

Its vapor-density was determined by the Hofmann method.

0.1221 gram of the oil gave 68.5 cc. of vapor at 182°, and under a tension of 352.8 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.91	4.91

Although the composition as shown by analysis seemed to be sufficient to demonstrate the presence of a hydrocarbon at this point, evidently analytical data alone would be insufficient, unless supported by a constant boiling-point. The distillate used in the determination described above was obtained after a long fractional separation, but without purification, except the removal of sulphur compounds, until after the distillations were made. To prove beyond question the constancy in boiling-point, another portion of the crude distillate after the fifteenth distillation was thoroughly agitated and warmed with fuming sulphuric acid, washed, dried, and the distillation continued fourteen times longer. About 100 grams of the oil collected so that it distilled at 163°–164°, mostly at 164°, under a tension of 760 mm., and with the mercury column all in the vapor. There seems, therefore, to be no reasonable doubt that Pennsylvania petroleum contains a decane with this boiling-point. That this hydrocarbon is a decane is shown also by a determination of its molecular weight by the Beckmann method, which gave 142; and the formula $C_{10}H_{22}$ requires 142.

In forming the chlorine derivative of the hydrocarbon $C_{10}H_{22}$ (boiling-point 163°–164°) from Pennsylvania petroleum 45 grams of the purified hydrocarbon was subjected to the action of chlorine in sunlight with a sheet of paper interposed, until it increased in weight 17 grams. The chlorine was delivered rapidly above the oil, and it was absorbed as fast as it could be added. Hydrochloric acid escaped with effervescence, and the rapidity of the reaction generated sufficient heat to maintain the temperature in the vicinity of 70°. With a slower stream of chlorine in other experiments the heat was dissipated without heating the oil, although the chlorine was as readily absorbed. Without further treatment, the chlorine product was subjected to fractional distillation *in vacuo* under tension of 80 mm. After ten distillations, approximately 6 grams collected at 125°–130°, which determinations of chlorine, carbon and hydrogen showed to be monochlordecane :

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[1] Ann. chim. phys. [4], 1, 62.

I. 0.2181 gram of the oil gave 0.5460 gram CO_2, and 0.2265 gram H_2O.

II. 0.2024 gram of the oil gave 0.1660 gram AgCl.

	Calculated for $C_{10}H_{21}Cl$.	Found. I.	II.
C	68.00	68.23	....
H	11.90	11.55	....
Cl	20.11	....	20.29

The specific gravity of this chlordecane at 20° was 0.8914. The specific gravity of the same product, separated by Pelouze and Cahours, was not given. The chlordecanaphtene prepared by Markownikoff and Oglobine,[1] from decanaphtene boiling at 160°–162°, had the specific gravity 0.9390 at 0°. It boiled at 205°–206° (cor.). Chlordecane obtained by Pelouze and Cahours boiled under atmospheric pressure at 200°–204°. Our chlordecane could not be distilled under atmospheric pressure without decomposition. As nearly as its boiling-point could be determined, it distilled at 197°–203°.

On account of the small quantity of the chlorine derivatives described in this paper, the specific-gravity determinations may not be strictly accurate. But the errors are doubtless small, and they do not affect the value of the determinations in establishing the identity of these derivatives.

In continuing the distillation of the higher chlorinated products from the decane (boiling-point 163°–164°) of Pennsylvania petroleum, approximately 15 cc. of an oil collected after the eighth distillation, at 160°-170°, that was heavier than water. Even these high distillates, which could not be heated to their boiling-points without decomposition, could be distilled *in vacuo* with little, if any, decomposition. This product gave, on analysis, the values required for dichlordecane :

I. 0.2293 gram of the oil gave 0.4829 gram CO_2, and 0.1884 gram H_2O.

II. 0.2557 gram of the oil gave 0.3420 gram AgCl.

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[1] Ann. chim. phys. [6], 2, 453.

	Calculated for $C_{10}H_{20}Cl_2$.	Found. I.	Found. II.
C	56.87	57.42	....
H	9.48	9.13	....
Cl	33.65	....	33.09

This dichlordecane gave 1.0187 as its specific gravity at 20°.

Decane, $C_{10}H_{22}$, 173°–174°.

Above 163° (730 mm.) the distillates were small in amounts to 168°, where they began to increase, and large quantities collected within degree limits to 173°, when they again fell off to small volumes. The fraction 169°–170° was selected for examination, which included analyses of the crude distillate, analyses after purification with acids, and the formation of the chlorine derivatives. It is interesting to note that unpurified distillates give percentages of carbon and hydrogen corresponding to the series C_nH_{2n}, or to numbers between this series and the series C_nH_{2n+2}. The unpurified distillate 169°–170° (730 mm.) gave the following results:

0.1521 gram of the oil gave 0.4758 gram CO_2, and 0.2018 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Calculated for $C_{10}H_{20}$.	Found.
C	84.51	85.71	85.31
H	15.49	14.29	14.72

The specific gravity of this distillate at 20° was found to be 0.7502. Its vapor-density, determined by the Hofmann method, gave the following value:

0.1533 gram of the oil gave 74.6 cc. of vapor at 182°, under a tension of 414.6 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.92	4.86

Evidently no particular value can be attached to such determinations of vapor-density, since, as shown by analysis, the oil is not composed of a single body. The same is true of boiling-points unsupported by other values. The contaminating body frequently has the same or nearly the same boiling-point as the principal constituent, and after the removal of the impurity the boiling-point is not materially changed. Another portion of the crude distillate was shaken with ordinary strong sulphuric acid, washed with caustic soda, water, and dried with sodium.

I. 0.1476 gram of this oil gave 0.4586 gram CO_2, and 0.1980 gram H_2O.

II. 0.1674 gram of this oil gave 0.5190 gram CO_2, and 0.2263 gram H_2O.

	I.	II.
C	84.72	84.57
H	14.90	15.03

The specific gravity of this oil was 0.7486. Its vapor-density was determined: 0.1454 gram of the oil gave 73 cc. of vapor at 182°, under a tension of 410 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.92	4.75

Another portion of the crude distillate was agitated with a mixture of nitric and sulphuric acids. An oily nitro product separated above the acids, which became partially crystalline on standing. It was doubtless a nitro derivative of cymol (boiling-point of metacymol 174°–176°, of paracymol 171°–172°).

The quantity of the nitro product was small, and the proportion of cymol was still further shown to be very small by treatment with fuming sulphuric acid. 185 grams of the distillates 167°–170°, after the eighteenth distillation, first by agitation in the cold, and then by warming to 125°, gave a loss in weight of only 15 grams, or about 8 per cent. of the weight taken. A barium salt was formed of the sulphonic acid, but it appeared as a thick gummy mass, so uninviting that nothing further was done with it. The purification with fuming sulphuric acid was intended more especially to show whether the boiling-point of the distillates would be materially affected. But the only difference observed was that they came together more readily and completely within one degree, 169°–170°, under 730 mm., and at 173°–174°, chiefly at 174°, under a tension of 760 mm., with the mercury column all in the vapor. It is interesting to observe how slightly the boiling-point was affected by the removal of the contaminating bodies. Evidently, the principal influence of the latter was in preventing the hydrocarbon from collecting closely at its true boiling-point.

The remaining oil was boiled with sodium as long as the metal was affected, and until it remained unchanged on standing with the oil. Even after this treatment was repeated several times, the percentage of carbon was somewhat too high and of hydrogen too low.

0.1503 gram of the oil gave 0.4664 gram CO_2, and 0.2050 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.65
H	15.49	15.14

After this purification the specific gravity obtained was 0.7475. For still further certainty as to the purity and composition of this distillate another portion was warmed during several hours with fuming sulphuric acid and shaken thoroughly. After washing and standing over sodium it was analyzed:

0.1754 gram of the oil gave 0.5431 gram CO_2, and 0.2442 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.45
H	15.49	15.47

In the latter treatment the acid solution, when neutralized with baric carbonate, gave a barium salt in clusters of needles, sparingly soluble in water, doubtless the barium salt of cymolsulphonic acid, although the quantity obtained was too small for analysis.

After this prolonged treatment with the fuming acid, the specific gravity was found to be 0.7467, substantially the same as in the previous determinations, and practically the same as the specific gravity of the decane boiling at 163°.

The molecular weight of this hydrocarbon, as determined by the Beckmann method, using benzol as a solvent, was found to be 144; since the formula $C_{10}H_{22}$ requires 142, this determination leaves no doubt that this body is decane, and not a higher homologue.

The chlorine derivatives of the decane boiling at 173°–174° were formed in the same manner as those of its isomer.

grams of the purified distillate was allowed to absorb 9 grams of chlorine, and the product was fractioned *in vacuo*. After the fourth distillation a small quantity collected at 130°–140°, which gave the percentages of carbon, hydrogen, and chlorine required for monochlordecane.

I. 0.2082 gram of the product gave 0.1699 gram AgCl.

II. 0.2003 gram of the product gave 0.5038 gram CO_2, and 0.2150 gram H_2O.

	Calculated for $C_{10}H_{21}Cl$.	Found. I.	II.
C	68.00	....	68.61
H	11.90	....	11.93
Cl	20.11	20.19	....

The specific gravity of this chlordecane at 20° was 0.8874, a value somewhat lower than the specific gravity of the chlordecane formed from the decane boiling at 163°, *viz.*, 0.8914. After the study of its other properties not enough of this chlordecane remained for a determination of its boiling-point under atmospheric pressure. As the specific gravity of the chlorine derivative of petroleum decane, Lemoine[1] gave 0.908. This value must have been obtained from decane boiling at 162°, since the French chemists have never recognized a decane in petroleum boiling at 173°. It was probably obtained in an impure product, since it is very considerably higher than our determination, which was made, as already shown, in chlordecane from well purified decane.

In continuing the vacuum-distillation of the chlorine products from the decane boiling at 173°, a considerable quantity collected at 170°–171°, 80 mm., which distilled at 235°–240°, 747 mm. Its composition was shown by analysis.

0.2008 gram of the oil gave 0.4121 gram CO_2, and 0.1641 gram H_2O.

0.2540 gram of the oil gave 0.3532 gram AgCl.

	Calculated for $C_{10}H_{20}Cl_2$.	Found. I.	II.
C	56.87	55.96	....
H	9.48	9.08	....
Cl	33.65	....	34.38

This substance is, therefore, dichlordecane. The quantity obtained was barely sufficient for a determination of its specific gravity ; it gave at 20°, 1.0126.

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[1] Bull. Soc. chim., (Paris), **41**, 165.

The presence of a decane at 174° seems therefore to be established in Pennsylvania petroleum, confirming the observations of Warren, who alone of all those who have examined American petroleum found a body at this point. If Pelouze and Cahours had carried their course of distillations sufficiently far, they could not have failed to discover this body, since it forms such a large proportion of the higher boiling petroleum distillate. Those chemists did, however, collect a distillate at 180°-182°, which gave analytical values and a vapor-density very closely supporting the formula $C_{11}H_{24}$. For some time I was in doubt as to whether a distillate might not persist at this point, and it was only after a prolonged series of separations that it was possible to separate the distillates, 180°–182°, entirely into higher and lower limits, thus supporting the conclusion of Warren, that Pennsylvania petroleum contains no hydrocarbon in appreciable quantity boiling in the vicinity of 180°.

Hendecane, $C_{11}H_{24}$, 196°.

As the boiling-point rose, the distillates showed less stability, as indicated by more color in the residue in a long course of distillations, although this was not sufficient to interfere with the collection of a homogeneous body within narrow limits of temperature. Between 189° and 192° distillates early began to accumulate, and the quantity gradually increased until 150 cc. was obtained, which distilled entirely at 190°–191, under 730 mm.

On standing over sodium, a portion of this distillate deposited a reddish flocculent precipitate in very appreciable quantity, which indeed was observed in all unpurified distillates. On this account very little importance has been attached to the composition of these oils, as shown by analysis, except to demonstrate what slight weight can be given to those results. Drying with sodium is indispensable, on account, as shown in another connection, of the difficulty in removing water by other means.

Determinations of carbon and hydrogen in the crude distillate, 190°–191°, dried over sodium, gave the following results:

0.1521 gram of the oil gave 0.4787 gram CO_2, and 0.1972 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.71	85.82
H	14.29	14.41

The specific gravity at 20° was found to be 0.7673. After thorough agitation with sulphuric acid and washing with sodic hydrate and water, the specific gravity was scarcely affected, 0.7662.

A comparison of the composition and specific gravity of the crude distillate, 190°–191°, 730 mm., as shown above, with the results of Warren and those of Pelouze and Cahours, in connection with what follows after further purification, reveals the cause of the lack of uniformity in the earlier work. The specific gravity of Warren's analyzed product, 0.7721 at 15°, which was only purified by boiling with sodium, is substantially the same as that of Pelouze and Cahours, 0.7780 at 20°, which was purified with concentrated sulphuric acid and sodic carbonate, but appreciably higher than the specific gravity of our crude distillate, only dried over sodium. The percentage-composition of these products purified in this manner may be more clearly understood if the results of analysis are brought together, as in the following table:

	Warren.		Mabery.	Pelouze and Cahours.	
	I.	II.		I.	II.
C	85.60	85.33	85.82	84.79	84.58
H	14.80	14.65	14.41	15.42	15.36

Required for

	$C_{11}H_{22}$.	$C_{11}H_{24}$.	$C_{12}H_{26}$.
C	85.72	84.62	84.70
H	14.29	15.38	15.30

It is difficult to see how results so closely supporting the formula C_nH_{2n+2} as those of Pelouze and Cahours could be obtained in a product still containing aromatic hydrocarbons, as shown by their method of purification and by the higher specific gravity. In the case of this particular hydrocarbon, the method of purification is not especially mentioned, but their general method, which is mentioned under nearly every other member of the long series of hydrocarbons which they examined, consisted in agitating the oil in the cold with concentrated sulphuric acid and washing with sodic carbonate. Then their method included no special means of drying the oil for analysis. It is quite impossible to remove moisture entirely from these hygroscopic oils without the aid of the most vigorous desiccating agents. Nothing less than standing continuously over sodium, in my experience, will insure a perfectly dry condition.

It is evident from the following description of their experiments that Pelouze and Cahours tried the action of reagents on their oil, although they seem not to have suspected the presence of an aromatic hydrocarbon C_nH_{2n-6}: "Le brome, l'acide azotique fumant, l'acide sulfurique au maximum de concentration et l'acide azotique de Nordhausen ne l'attaquent pas à froid. Le mélange des acides azotique et sulfurique agit sur le carbure lorsqu'on maintient ces corps pendant quelque temps en ébullition. Prolonge-t-on l'action, on voit se former une petite quantité d'un produit solide et crystallisable. Il se sépare en même temps une huile jaunâtre un peu plus dense que l'eau. De plus, on dèmêle dans les vapeurs nitreuses l'odeur caractéristique des acides volatils homologues de l'acide acétique."

Upon agitation with nitric and sulphuric acids, the distillate 190°–191° deposited a heavy nitro compound.

Our observations concerning the action of a mixture of concentrated nitric and sulphuric acids in the cold on this distillate do not coincide with those of Pelouze and Cahours. Immediately, upon vigorous agitation, a heavy nitro compound separated as a heavy oil, forming a crystalline product on standing. 20 grams of the oil lost 4.5 grams by this treatment, equivalent to 22 per cent. of its weight. The nitro compound was very sparingly soluble in hot alcohol, from which it crystallized in needles, melting at 169°–170°. As will be seen later, nitro compounds with the same melting-points were separated from Ohio and Canadian petroleum, which do not correspond in melting-point to that of either dinitrodurol, 205°, nor of dinitroisodurol, 156°, although crystallization was continued until the melting-point was pretty constant. It would have been interesting to obtain sufficient of this substance for more complete examination; but, with the great amount of work on hand in connection with the principal hydrocarbons, it did not seem best to allow our attention to be diverted from the main object in view. It should not be understood that the diminution in weight mentioned above, on treating with acids, was due entirely to the removal of aromatic hydrocarbons. In all the petroleum hydrocarbons we have separated, on treating with nitric and sulphuric acids, a large proportion of the products has remained in solution, and it has been possible to reduce them only very slowly by heating with sodium. From the distillates above 150°, heavy dark brown precipitates have been formed at first, followed by light flocculent deposits resembling aluminic hydrate. On distilling after treating with sodium, usually a considerable residue is left. If heating with sodium be continued until there is no further action, the metal will remain bright in the oil, and we have looked on this as an indication of purity.

The oil separated from the acid mixture was boiled with sodium until it produced no further decomposition, shaken with sulphuric acid, and allowed to stand a long time in contact with sodium. Since the metal remained unaffected, the oil was assumed to be completely purified; nevertheless, analysis showed still remaining a trace of the less hydrogenized body:

0.1547 gram of the oil gave 0.4816 gram CO_2, and 0.2104 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found.
C	84.63	84.87
H	15.38	15.12

A determination of the specific gravity of the purified oil gave 0.7585.

To prove with greater certainty the composition of this hydrocarbon, the crude distillate obtained, as described above, was heated on the steam-bath with fuming sulphuric acid, which caused some decomposition, and the oil remaining washed thoroughly with caustic soda and water. 20 grams of the crude distillate gave 16.5 grams of the purified oil, with a loss of 17.5 per cent., which is probably an approximate measure of the proportion of aromatic hydrocarbons in this distillate. It is probable that the loss in weight with the mixture of nitric and sulphuric acids included some decomposition of the principal hydrocarbon. The oil treated with fuming sulphuric acid was carried through ten distillations, after which it collected for the most part within one degree, and 100 grams distilled at 196°–197°, under 760 mm., and with the mercury column all in the vapor. This product was again warmed with fuming sulphuric acid, washed, and dried over sodium.

In the latter experiment the acid was only slightly discolored. The oil gave the faint characteristic odor of these hydrocarbons, which is easily recognized when the impurities are removed. It then gave percentages of carbon and hydrogen required for a hydrocarbon of the series $C_n H_{2n+2}$.

I. 0.1502 gram of the oil gave 0.4665 gram CO_2, and 0.2090 gram H_2O.

II. 0.1661 gram of the oil gave 0.5157 gram CO_2, and 0.2322 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found.	
		I.	II.
C	84.62	84.70	84.67
H	15.38	15.46	15.53

The specific gravity of the oil 196°–197°, after purification in this manner, was found to be 0.7581. The close agreement in specific gravity of the products after treatment with the mixture of nitric and sulphuric acids, and with fuming sulphuric acid, as well as the proportions of carbon and hydrogen, indicate that the oil was quite thoroughly purified.

That the formula of the purified hydrocarbon boiling at 196° is $C_{11}H_{24}$, and not the next higher homologue, receives further support by a determination of its molecular weight, in which Mr. Hudson obtained, by the Beckmann method, the value 157; required for $C_{11}H_{24}$, 156.

In the preparation of the chlorine derivatives of the hydrocarbon $C_{11}H_{24}$, (boiling-point 196°) of Pennsylvania petroleum, 40 grams of the oil was allowed to absorb 14 grams of chlorine and the chlorine product was fractioned *in vacuo*. After five distillations, 10 cc. collected at 145°-150° (80 mm.), that distilled with decomposition at 225°-230°, bar. 747 mm. This product gave on analysis percentages of carbon, hydrogen, and chlorine required for $C_{11}H_{23}Cl$:

I. 0.2291 gram substance gave 0.1713 gram AgCl.

II. 0.1933 gram of the substance gave 0.4914 gram CO_2, and 0.2071 gram H_2O.

	Calculated for $C_{11}H_{23}Cl$.	Found. I.	Found. II.
C	69.29	....	69.30
H	12.07	....	11.91
Cl	18.13	18.49	....

The specific gravity of monochlorhendecane at 20° was found to be 0.8721. Pelouze and Cahours found that the hydrocarbon which they collected at 196°-200° absorbed chlorine at a gentle heat with the formation of a monochlor derivative that boiled at 242°-245° with a specific gravity of 0.9330 at 22°. These values are much in excess of the determinations given above. Our boiling-point under atmospheric pressure was only approximate, since the chlorine product was considerably decomposed at those temperatures. In the action of chlorine, the substitution proceeded with the greatest readiness as soon as the chlorine came in contact with the hydrocarbon. No heat was necessary, although, if the action proceeded rapidly, much heat was developed.

The composition of the product obtained by Pelouze and Cahours corresponds with the formula $C_{12}H_{25}Cl$, as shown by the following record of their analyses :

	Calculated for $C_{12}H_{25}Cl$.	Found.
C	70.41	70.34
H	12.23	12.37
Cl	17.36	17.53

In further support of the formula $C_{11}H_{23}Cl$, Mr. Hudson made a determination of the molecular weight of the chloride by the Beckmann method, using benzol as a solvent, in which he obtained 191 ; the formula $C_{11}H_{23}Cl$ requires 190.

Evidently a dichlorhendecane was also formed in the chlorination, since in the vacuum-distillation, about 5 cc. collected at 190°-200°, that gave a percentage of chlorine two per cent.

too low for the required value. But the quantity was too small to purify it sufficiently to give acceptable results.

Dodecane, $C_{12}H_{26}$, 214°–216°.

Above 193°, 730 mm., the fractions were very small to 208°, but between 208° and 210° much larger quantities collected, for the most part at 209° to 210°. Without further purification, except drying with sodium, the crude distillate was analyzed :

0.1392 gram of the oil gave 0.4355 gram CO_2, and 0.1845 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.71	85.33
H	14.29	14.73

A determination of its specific gravity gave 0.7745. After treatment with concentrated sulphuric acid, the specific gravity was not changed—0.7744. Another portion of the crude distillate was shaken with nitric and sulphuric acids, and allowed to stand several hours. After separation from the small quantity of the heavy nitro product and the acid, the oil was boiled with sodium until there was no further action, and the metal remained unaffected on standing several weeks. The oily nitro product deposited a small quantity of crystals on standing, but not enough to purify for a determination of its melting-point.

Purified in this manner, this distillate gave the following results on analysis :

I. 0.1547 gram of the oil gave 0.4816 gram CO_2, and 0.2104 gram H_2O.

II. 0.1474 gram of the oil gave 0.4562 gram CO_2, and 0.2017 gram H_2O.

	Calculated for $C_{12}H_{26}$.	Found.	
		I.	II.
C	84.72	84.87	84.41
H	15.28	15.12	15.21

Its specific gravity at 20° was found to be 0.7684.

Another portion of the crude fraction, 209°–210°, purified by thorough agitation and warming with fuming sulphuric acid, twice repeated, gave the following results on analysis :

0.1471 gram of the oil gave 0.4537 gram CO_2, and 0.2068 gram H_2O.

	Calculated for $C_{12}H_{26}$.	Found.
C	84.72	84.12
H	15.28	15.63

The specific gravity of the oil after treatment with the fuming acid was 0.7729, somewhat higher than the portion purified with nitric and sulphuric acids. It is quite possible that the purification with fuming sulphuric acid, in this instance, was not capable of removing the contaminating bodies as thoroughly as the other method. The purified hydrocarbon was found to distil completely at 214°–216°, under a tension of 760 mm., and with the mercury column all in the vapor. A determination of its molecular weight by the Beckmann method gave Mr. Hudson 173; required for the formula $C_{12}H_{26}$, 170.

In the formation of the chlorine derivatives from the hydrocarbon $C_{12}H_{26}$, Pennsylvania petroleum, 95 grams of the purified hydrocarbon was exposed to the action of chlorine until 30 grams was absorbed. Apparently chlorine substitutes as readily in the hydrocarbons of higher, as in those of lower, boiling-points. In fractioning under 80 mm. after six distillations, about 20 cc. collected at 142°–153°, which distilled at 230°–235° atmospheric pressure. In none of the distillates of chlorine derivatives was hydrochloric acid detected as a product of decomposition when distilled *in vacuo*. Under atmospheric pressure it was impossible to carry on these distillations without serious decomposition. The composition of this fraction corresponded to that of $C_{12}H_{25}Cl$.

I. 0.1910 gram of the oil gave 0.1385 gram AgCl.

II. 0.1339 gram of the oil gave 0.3434 gram CO_2, and 0.1423 gram H_2O.

	Calculated for $C_{12}H_{25}Cl$.	Found.	
		I.	II.
C	70.42	....	69.93
H	12.23	....	11.81
Cl	17.36	17.93	....

In determining the specific gravity of this chlorine derivative at 20° it gave 0.8919. A determination of its molecular weight by the Beckmann method, with benzol as a solvent, gave Mr. Hudson 200; required for $C_{12}H_{25}Cl$, 204. The chloride formed by Pelouze and Cahours from their distillate 216°–218° boiled at 258°–260°, somewhat higher than the boiling-point of their chloride described in this paper. From the results of their analyses, they deduced the formula $C_{13}H_{27}Cl$.

The chlorination of this product was not carried far enough to form sufficient of the dichlor derivative to separate it by distillation. The greater part of the oil after chlorination distilled at 212°–214°, the boiling-point of the hydrocarbon.

A description of these experiments, which are intended to establish the composition of the hydrocarbon distilling at 214°–216°, should not be concluded without a statement of the relation they sustain to those of Warren and of Pelouze and Cahours, the only experimenters who have hitherto attempted the separation of this constituent from American petroleum. The two determinations most nearly concerned in this discussion are specific gravity and percentage composition. In the following comparison of specific-gravity determinations and percentage composition, it should be borne in mind that Warren purified his distillate only by boiling with metallic sodium, Pelouze and Cahours by agitation with concentrated sulphuric acid and washing with sodic carbonate; with those results are brought together the determinations described in this paper in the crude distillate, after agitation with concentrated sulphuric acid, and after more thorough purification with the acid mixture:

	Warren, 15°.		Pelouze and Cahours, 20°.		Mabery, 20°.			
					Crude distillate.	Agitation with H_2SO_4.	Purified.	
Sp. gr.	0.7804		0.7960		0.7745	0.7744	0.7684	
	I.	II.	I.	II.			I.	II.
C	84.66	85.74	84.58	84.51	85.33		84.87	84.41
H	14.85	14.66	15.37	15.45	14.73		15.12	15.21

The percentages of carbon and hydrogen required for the formula $C_{12}H_{26}$ are: C, 84.72; H, 15.30; for the formula $C_{13}H_{28}$: C, 84.78; H, 15.22. Evidently the differences in percentage-composition are not sufficient to determine by analysis alone which of the two formulas is the correct one. But the differences between either of these formulas and the formula $C_{12}H_{24}$(C, 85.71; H, 14.29) should be readily shown by analysis.

Having at hand a portion of the purified distillate (214°–216°) that had been treated with chlorine and the part not chlorinated distilled, I continued the distillation until the chlorine derivatives were completely removed, and the hydrocarbon was then treated with fuming sulphuric acid and distilled over sodium. It then gave as its specific gravity 0.7749, substantially the same as before chlorination. Normal dihexyl prepared by the action of zinc and hydrochloric acid on normal hexyl iodide boils at 214°.5 and apparently is identical with a hydrocarbon having the same composition, obtained by electrolysis of potassium œnanthylate (Schorlemmer). The latter has the specific gravity 0.7738 at 17°. It is therefore probable that the hydrocarbon $C_{12}H_{26}$, boiling at 214°–216°, from American petroleum, has the same form. The purified hydrocarbon then gave the following percentages of carbon and hydrogen:

I. 0.1599 gram of the oil gave 0.4978 gram CO_2, and 0.2177 gram H_2O.

II. 0.1617 gram of the oil gave 0.5021 gram CO_2, and 0.2270 gram H_2O.

III. 0.1559 gram of the oil gave 0.2193 gram H_2O. The CO_2 was lost.

	Calculated for $C_{12}H_{26}$.		Found	
		I.	II.	III.
C	84.72	84.89	84.69	....
H	15.28	15.10	15.31	15.63

The results indicate the absence of any impurity not readily acted on by chlorine.

As one of the results of this examination it can, I think, be safely asserted that the constituents of Pennsylvania petroleum with boiling-points at 163°–164°, 173°–174°, 196°–197°, and at 215°–216°, constitute the main body of this petroleum within these limits, and whatever other bodies may be present, they are to be found only in comparatively small quantities. As to the proportion of aromatic hydrocarbons in the crude oil, no direct estimation can be based on these observations.

Fuming sulphuric acid removed 40 per cent. of the crude distillate 160°–161°, leaving decane as the remaining 60 per cent. Whether the portion removed was mesitylene alone may be questionable, but no doubt it formed the larger part of the body uniting with the fuming acid. Even in such prolonged fractional separations as those described in this paper, it cannot be assumed that nearly all the decane 163°–164° was collected in the fractions which should contain it, neither is it probable that the crude distillate from which was selected the specimen for the separation of these constituents contained all the decane in the corresponding quantity of crude oil. But it is evident that the aromatic hydrocarbons are present in no inconsiderable amounts, and without doubt these bodies have much influence on the illuminating qualities of the oil. As shown by the slight changes in specific gravity after the action of ordinary concentrated sulphuric acid, the action of this acid in the usual method of refining does not include to any considerable extent the removal of the aromatic hydrocarbons. Its beneficial action seems to concern more especially the decomposition-products of distillation and certain constituents present in minute quantities, such as the unsaturated hydrocarbons, the oxygen, and nitrogen compounds. It scarcely need be mentioned that this applies to the action of sulphuric acid in the cold. When heated, without doubt a part of the aromatic hydrocarbons would be removed, to the detriment of the burning qualities. The formation of barium salts from all the distillates treated with fuming sulphuric acid proves the presence in appreciable amounts of a wide range of aromatic hydrocarbons.

Without reference to the percentages of carbon and hydrogen, the low specific gravity of the hydrocarbons described above is sufficient to show that they are not naphtenes. The following comparison of the unpurified distillates and the purified hydrocarbons as regards their specific gravity with the naphtenes separated by Markownikoff from the Russian oil will perhaps make these differences more clearly understood.

Baku naphtenes :

	B. P.	Specific gravity.
$C_{10}H_{20}$	160°–162°	0.795 (0°)
$C_{11}H_{22}$	180°–182°	0.8119 (0°)
$C_{12}H_{24}$	196°–197°	0.8055 (14°)

Pennsylvania hydrocarbons, $C_n H_{2n+2}$:

		Specific gravity at 20°.	
	B. P.	Purified.	Unpurified.
$C_{10}H_{22}$	163°–164°	0.7479	0.7684
$C_{10}H_{22}$	173°–174°	0.7467	6.7502
$C_{11}H_{24}$	196°–197°	0.7381	0.7673
$C_{12}H_{26}$	214°–216°	0.7676	0.7745

Another important result of this study is the evidence that the main body of the hydrocarbons in Pennsylvania petroleum within these limits of temperature are members of the series $C_n H_{2n+2}$. Satisfactory analytical data in proof of this conclusion have cost a vast expenditure of time and effort, not only in the routine labor of separation and purification, but in obtaining sufficiently close percentages of carbon and hydrogen. In such a large number of determinations the ordinary method of combustion becomes exceedingly tedious, since all details must be watched with the greatest care. In the early part of the analytical work there was not the slightest evidence as to whether the hydrocarbons were of the series $C_n H_{2n+2}$, or of the series $C_n H_{2n}$. The extreme hygroscopic nature of these bodies was not then appreciated, nor the refinement in purification necessary to yield accurate results. Many analyses were made before these details were fully understood.

Constituents of Ohio Trenton Limestone Petroleum.

The constituents of Ohio petroleum between 160° and 216° were sought for in vacuum-distillates obtained from the crude oil, as described in a former paper.[1]

Distillation *in vacuo* was continued until all portions had collected that could be brought together within the desired limits. Further concentration was carried on under atmospheric pressure, since this did not occasion serious decomposition. Probably no petroleum distillates with such high boiling-points can entirely escape decomposition in a long course of distillations, but small amounts of decomposition-products can no doubt be removed by sulphuric acid, leaving the main body of the oil free from contamination. After the first distillations *in vacuo*, Ohio distillates seem to suffer no more change during distillation than those from Pennsylvania oil. Before separation into two-degree fractions, the sulphur compounds were removed as far as possible by precipitation with mercuric chloride. As the distillations proceeded, the characteristic "heaps" began to appear in the vicinity of 160°, 730 mm., falling off below 158° and above 163°. These portions were therefore carried through a long course of separations, fifty altogether, forty-five within one degree, after which they collected mainly at 159°–162°. A combustion of the crude distillate 159°–160°, purified as explained above only by mercuric chloride, gave the following results:

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[1] This JOURNAL, **17**, 739.

I. 0.1591 gram of the oil gave 0.4983 gram CO_2, and 0.2076 gram H_2O.

	Calculated for		
	$C_{10}H_{20}$.	$C_{10}H_{22}$.	Found.
C	85.71	84.51	85.41
H	14.29	15.49	14.50

On the basis of these values alone, there should be no hesitation in assigning to this oil the formula $C_{10}H_{20}$. The specific gravity of this distillate was found to be 0.7717. Its vapor-density was determined by the Hofmann method:

0.1272 gram of the oil gave 67 cc. of vapor at 182°, and under a tension of 374.4 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.92	4.96

After treatment with ordinary concentrated sulphuric acid, another portion of this distillate gave 0.7678 as its specific gravity, and the following percentages of carbon and hydrogen:

0.1416 gram of the oil gave 0.4452 gram CO_2, and 0.1855 gram H_2O.

C	85.76
H	14.56

Agitation of the crude distillate in the cold with a mixture of concentrated nitric and sulphuric acids caused the separation of a heavy oil that deposited crystals of a nitro product on standing. After crystallization from hot alcohol, in which it is sparingly soluble, this substance melted at 229°, showing it to be trinitromesitylene (melting-point 230°–232°). Complete removal of the nitro compound from decane required prolonged boiling with sodium followed by agitation with sulphuric acid. The hydrocarbon then no longer attacked the metal, nor tarnished it on long standing. Purified in this manner, this oil gave values required for decane:

0.1512 gram of the oil gave 0.4677 gram CO_2, and 0.2088 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.35
H	15.49	15.35

For further assurance as to the composition of this hydrocarbon, another portion of the crude distillate was first agitated in the cold with fuming sulphuric acid, which produced no heat, and then heated with the acid on the steam-bath. As in most of the crude oils when treated in this manner, the acid turned dark when heated, and evidently extracted a considerable proportion of the oil. After washing with sodic hydrate and water, the remaining oil gave only the faint odor characteristic of the petroleum hydrocarbons. In many of the analyses it will be seen that the percentage of hydrogen is somewhat lower than is required by a pure substance. This deficiency is doubtless due to a very small proportion of the hydrocarbon with less hydrogen, the last traces of which it is somewhat difficult to remove. The fraction 160°–162°, after the last purification, contained the following percentages of carbon and hydrogen:

0.1532 gram of the oil gave 0.4740 gram CO_2, and 0.2113 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.38
H	15.49	15.33

A determination of its specific gravity at 20° gave 0.7535, a value slightly higher than the specific gravity of the corresponding fraction of the Pennsylvania oil, doubtless due to the slight trace of impurity still remaining. In determining the molecular weight of this decane by the method of Beckmann, Mr. Hudson obtained 145; required for $C_{10}H_{22}$, 142.

The boiling-point of this hydrocarbon, so thoroughly purified that neither fuming nitric acid nor fuming sulphuric acid produced further change, was found to be nearly the same as that of the decane (boiling-point 163°) from Pennsylvania petroleum. 50 cc. distilled entirely between 162°.5 and 163°.5, under a barometric pressure of 757.5 mm.

Since even a larger proportion of the crude distillate was removed in combination with fuming sulphuric acid than from the Pennsylvania distillate, 163°, an attempt was made to ascertain the composition of the barium salt, formed by neutralizing with baric carbonate and crystallizing the filtered solution, after boiling with bone-black. A considerable quantity of the barium salt crystallizing in needles was obtained, and the percentage of barium found (25.95) agreed closely with the theoretical percentage of barium in barium mesitylenesulphonate, $(C_9H_{11}SO_3)_2Ba$ (25.61). But the salt proved to be anhydrous, while according to Jacobson[1] barium mesitylenesulphonate crystallizes with $9H_2O$. On account of the limited supply of the barium salt, it was not possible to verify this determination by further study; but there can be no doubt of the possibility of forming a barium salt of mesitylenesulphonic acid in this manner, since trinitromesitylene melting at 225°–230 (melting-point of trinitromesitylene, 230°) was formed without difficulty by the action of fuming nitric acid on this distillate.

As further evidence of the composition of the hydrocarbon, 163°, Ohio petroleum, 46 grams well purified with fuming sulphuric acid was exposed to the action of chlorine until the weight had increased 11 grams. The chlorinated product was fractioned twelve times under 80 mm., when 15 cc. collected at 130°–135°, distilling at 200°–208°, atmospheric pressure. It was shown by analysis to have the composition required for $C_{10}H_{21}Cl$.

I. 0.2340 gram of the substance gave 0.1934 gram AgCl.

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[1] Ann. Chem. (Liebig), **146**, 98.

II. 0.1935 gram of the substance gave 0.4785 gram CO_2, and 0.2119 gram H_2O.

III. 0.1715 gram of the oil gave 0.4246 gram CO_2, and 0.1963 gram H_2O.

	Calculated for $C_{10}H_{21}Cl$.	Found. I.	II.	III.
C	68.00	....	67.44	67.53
H	11.90	....	12.17	12.73
Cl	20.11	20.45	....	....

In a determination of its specific gravity at 20°, this chlordecane gave 0.8958. In continuing the distillation of the chlorine product after the twelfth fraction, 10 cc. collected at 160°–170°, specific gravity 1.0627 at 20°, which gave the percentages of carbon, hydrogen, and chlorine required for $C_{10}H_{20}Cl_2$:

I. 0.2984 gram of the substance gave 0.4105 gram AgCl.

II. 0.2753 gram of the substance gave 0.5746 gram CO_2, and 0.2356 gram H_2O.

	Calculated for $C_{10}H_{20}Cl_2$.	Found. I.	II.
C	56.87	....	56.94
H	9.47	....	9.51
Cl	33.65	34.03	....

Normal Decane, B. P. 173°–174°.

Above 162° (730 mm.) the distillates were small to 168°. After long continued distillation, 300 grams collected at 169°–170° (730 mm.), which, without further purification, except drying over sodium, gave the following percentages of carbon and hydrogen:

I. 0.1434 gram of the oil gave 0.4486 gram CO_2, and 0.1927 gram H_2O.

II. 0.1577 gram of the oil gave 0.4948 gram CO_2, and 0.2070 gram H_2O.

	Calculated for $C_{10}H_{22}$.	$C_{10}H_{20}$.	Found. I.	II.
C	84.51	85.71	85.33	85.55
H	15.49	14.29	14.94	14.58

A determination of the specific gravity of this distillate gave 0.7621, a value considerably higher than that of the corresponding unpurified Pennsylvania distillate, 0.7502.

0.1670 gram of the oil gave 79 cc. of vapor at 182°, under a tension of 366 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.90	5.15

A portion of the crude distillate was shaken with concentrated sulphuric acid, washed, and dried for analysis:

0.1504 gram of the oil gave 0.4708 gram CO_2, and 0.1984 gram H_2O.

C	85.37
H	14.67

The specific gravity of this oil, after treatment with sulphuric acid, was somewhat lower than that of the crude distillate, 0.7580. A determination of its vapor-density gave 5.02. The fraction 169°–170°, Ohio oil, was the first to be submitted to the action of the mixture of nitric and sulphuric acids. When a small quantity of the oil was heated to about 125° during twenty-four hours with the acid mixture, nitrous fumes were freely evolved and the volume of the oil gradually diminished until very little remained. Upon diluting the acid, a heavy, tarry mass was precipitated, evidently a product of decomposition of the hydrocarbon. In another experiment, 24 grams of the crude distillate were agitated in the cold with the acid mixture, separated from the acid and the oily nitro product, washed, and dried. After boiling with sodium and shaking with sulphuric acid, there remained only 17 grams, there having been a loss of 32 per cent. A portion of the nitro product crystallized on standing, and after several crystallizations from hot alcohol, in which it was sparingly soluble, the melting-point could not be raised above 164°–165°. In testing the action of sulphuric acid alone on the distillate 171°–172°, 25 grams of the crude oil was agitated with three successive portions of concentrated sulphuric acid, washed with sodic hydrate and water, and dried. In the first treatment, in which the oil lost in weight 1.8 grams, the acid was badly discolored ; the subsequent portions were not affected. The oil was next heated gently with fuming sulphuric acid with agitation, which caused considerable blackening, washed first with concentrated sulphuric acid, then with sodic hydrate and water, and dried. After the last treatment, the oil weighed 19.8 grams, a loss of 25 per cent.

It is evident from these observations that some care is necessary in attempting to purify these hydrocarbons with concentrated nitric acid. In the cold or under a gentle heat, not prolonged, the decomposition is probably not serious. But at higher temperatures, as shown above, the action may proceed too far. The purified oil gave satisfactory results on analysis:

I. 0.1373 gram of the oil gave 0.4247 gram CO_2, and 0.1900 gram H_2O.

II. 0.1459 gram of the oil gave 0.4520 gram CO_2, and 0.2090 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.	
		I.	II.
C	84.51	84.36	84.47
H	15.49	15.38	15.92

Two determinations of the specific gravity at 20° of this oil in different preparations gave 0.7519 and 0.7513.

In a still more extended purification, some of the crude distillate was agitated thoroughly with the mixture of nitric and sulphuric acids, allowed to stand several hours with the acids, and, after washing, heated for some time with tin and hydrochloric acid. The washed and dried oil was then warmed with fuming sulphuric acid, washed, dried, and distilled. It then gave 0.7482 as its specific gravity at 20°, more nearly approaching the specific gravity of the Pennsylvania decane, 173°, 0.7467, and analysis indicated that the remaining oil had the composition of the general formula C_nH_{2n+2}:

0.1449 gram of the oil gave 0.4494 gram CO_2, and 0.2051 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.57
H	15.49	15.73

Another quantity of the crude distillate was heated on the steam-bath during several hours with fuming sulphuric acid, the acid being occasionally shaken with the oil, boiled with sodium, distilled, and dried for analysis:

0.1519 gram of the oil gave 0.4715 gram CO_2, and 0.2085 gram H_2O.

C	84.67
H	15.26

The specific gravity of this product was the same as before, 0.7514. In a determination of the molecular weight of the hydrocarbon purified by the mixture of nitric and sulphuric acids, tin and hydrochloric acid, fuming sulphuric acid, and sodium, Mr. Hudson obtained 142; required for $C_{10}H_{22}$, 142. The fuming sulphuric acid solution separated from the oil was neutralized with baric carbonate, filtered, and evaporated nearly to dryness. On cooling, a barium salt separated in needles, which were very sparingly soluble in cold water. The air-dried salt was anhydrous, and it gave, by ignition with sulphuric acid, 25.46 per cent. of barium. Hexahydrocymol requires 23.8 per cent. of barium, and isocymol 24.3. The first hydrocarbon boils at 171°–172°, *m*-cymol at 174°–176°, *p*-cymol at 172°–173°, and pseudocymol at 169°. By fuming sulphuric acid at least the isocymol, if present in petroleum, should be extracted, and it is probable that this barium salt was an impure compound of cymolsulphonic acid. That the decane boiling at 174° is the principal constituent of Ohio petroleum at this point, and that it contains a considerable proportion of aromatic hydrocarbons, has received ample proof. As to the precise form of the aromatic hydrocarbons, the quantity of material it has been expedient to manipulate in purifying the decane was not sufficient to demonstrate. It would evidently be impossible to separate these bodies from decane in any course of distillation, and it would require a large quantity of the crude distillate, although not so thoroughly distilled as the one prepared in this examination.

In still further evidence as to the formula of this hydrocarbon, the chlorine derivatives were prepared by the action of chlorine on a portion purified with the mixture of nitric and sulphuric acids and sodium. 83 grams of the hydrocarbon was allowed to absorb 30 grams of chlorine, the theoretical quantity for the mono derivative being 20 grams. As an illustration of the readiness with which substitution takes place, in this experiment the stream of chlorine happened to be exceptionally vigorous, but it was completely absorbed from the beginning to the extent of five grams during the first ten minutes. Hydrochloric acid escaped from the oil with brisk effervescence, although the chlorine was delivered at some distance above the surface of the oil. This rapid substitution at low temperature is quite unlike the substitution of chlorine in decanaphtene observed by Markownikoff and Oglobine, as shown by the following statement :[1] "Lorsqu'on fait agir du chlore sec sur les vapeurs du décanaphtène en ébullition et sous l'influence de l'insolation directe, la réaction se fait lentement avec dégagement d'acide chlorhydrique et demande un très grand excès de chlore en comparaison de ce qu'il en faut d'après le calcul théorique." Yet in the residue of the hydrocarbon not acted on by chlorine, Markownikof and Oglobine found a somewhat lower percentage of carbon and a higher percentage of hydrogen, from which, together with a slightly lower specific gravity, 0.792, than decanaphtene, 0.896, they infer that "ces chiffres semblent indiquer la prêsence d'une quantitê notable d'un hydrocarbure saturé." In accordance with my observations on all the hydrocarbons from Pennsylvania, Ohio, and Canadian oil which I have chlorinated, these bodies should be saturated long before the naphtenes, especially if the latter react slowly with chlorine at the boiling temperature.

In fractioning *in vacuo* under 80 mm. the chlorinated oil, after several distillations, about 8 cc. collected at 134°–136°, with a small proportion of unaffected hydrocarbon which came over at a lower temperature. Analyses of this product gave numbers corresponding to the composition of chlordecane:

I. 0.2773 gram of the oil gave 0.6977 gram CO_2 and 0.2886 gram H_2O.

II. 0.1623 gram of the oil gave 0.4085 gram CO_2, and 0.1679 gram H_2O.

III. 0.2117 gram of the oil gave 0.1707 gram AgCl.

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[1] Ann. chim. phys. (6), **2**, 453.

	Calculated for $C_{10}H_{21}Cl$.	Found. I.	II.	III.
C	68.00	68.60	68.54	....
H	11.90	11.56	11.50	....
Cl	20.11	....	....	19.93

A determination of the specific gravity of this chlordecane at 20° gave 0.8895. Under atmospheric pressure it distilled with some decomposition at 205°–210°. Its molecular weight, determined by the Beckmann method, was found by Mr. Hudson to be 174; required for the formula $C_{10}H_{21}Cl$, 176.5.

In continuing the fractional distillation *in vacuo* of the chlorine product from Ohio decane (boiling-point 173°) a small quantity, 3 cc., collected at 170°–180°, 80 mm., which distilled under atmospheric pressure at 240°–243°. On account of decomposition this portion was fractioned only five times, but it gave on analysis a percentage of chlorine corresponding to dichlordecane:

I. 0.2690 gram of the oil gave 0.5549 gram CO_2, and 0.2191 gram H_2O.

II. 0.2753 gram of the oil gave 0.5746 gram CO_2, and 0.2111 gram H_2O.

III. 0.3147 gram of the oil gave 0.4256 gram AgCl.

	Calculated for $C_{10}H_{20}Cl_2$.	Found. I.	II.	III.
C	56.87	56.24	56.94	....
H	9.48	9.04	8.51	....
Cl	33.65	....	....	33.46

A determination of the specific gravity of this dichlordecane at 20° gave 1.0300, which may not be strictly correct on account of the small quantity of the material.

In determining the boiling-point of this decane, 50 cc. of the oil, purified as thoroughly as possible, distilled at 173°.6–174°.6, mostly below 174°, under a tension of 760 mm. and with the mercury column all within the vapor.

The boiling-point of normal decane was given by Krafft[1] as 173° at 760 mm., but 0.7304, its specific gravity at 20°, is sensibly lower than that of the decane from petroleum. Whether this be due to the presence of a small amount of decanaphtene, which appears to be nearly inert toward the methods of purification that have been applied to these petroleum hydrocarbons, can only be determined by more extended experiments. In view of the ease in chlorination of the hydrocarbons, $C_n H_{2n+2}$, and the difficulty in chlorinating the naphtenes according to the experience of Markownikoff and Oglobine, perhaps fractional chlorination should permit of the removal of decane, and the naphtene would reveal its presence by analysis. As already shown in the case of Pennsylvania dodecane, the portion remaining after incomplete chlorination is the hydrocarbon $C_{12}H_{26}$.

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[1] Ber. d. chem. Ges., **15**, 1695.

Hendecane, $C_{11}H_{24}$, 195°–196°.

Above 173° (760 mm.), fractions collected irregularly and in small amounts to 188°. There was no indication of an accumulation in the vicinity of 180°, but after precipitation of the sulphur compounds with mercuric chloride considerable quantities collected at 188°–192° (730 mm.), which for the most part came together at 189°–191°. An analysis of the crude distillate gave the following percentages of carbon and hydrogen :

0.1444 gram of the oil gave 0.2536 gram CO_2, and 0.1888 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.71	85.67
H	14.29	14.53

A specific-gravity determination at 20° gave 0.7789, and a determination of its vapor-density by the Hofmann method the following value :

0.1286 gram of the oil gave 67 cc. of vapor at 182°, and under 357.5 mm.

Calculated for $C_{11}H_{22}$.	Found.
5.33	5.26

As in the corresponding crude Pennsylvania distillate, the percentage-composition of this hendecane based on the above analysis supports the formula $C_n H_{2n}$. Its specific gravity is nearly the same as that found by Warren, who gave the formula $C_n H_{2n}$; it is even closer to the value 0.7780, found by Pelouze and Cahours in their distillate from Pennsylvania, or rather from American petroleum. Pelouze and Cahours alluded to distillates prepared from Canadian petroleum, as well as from American petroleum, and their high specific gravity, much higher than Pennsylvania distillates yield, would seem to indicate that they had in hand Canadian distillates. Another portion of the crude distillate 189°–190° was agitated with a mixture of nitric and sulphuric acids, and allowed to stand some time after the heat of the first reaction had moderated. A heavy nitro compound separated, which crystallized on standing. The reaction was far more energetic than in the same distillate from Pennsylvania petroleum, probably on account of a larger proportion of aromatic hydrocarbons. A heavy nitro compound immediately separated as an oil, which crystallized on standing. It was purified by crystallization from alcohol, in which it was very sparingly soluble, and gave as its melting-point 158°–160°, which was not changed by several crystallizations. There are several aromatic hydrocarbons whose boiling-points are in this vicinity, but only one forms a nitro derivative with this melting-point, isodurol, whose trinitro derivative melts at 156°. It would be interesting to examine these nitro products more fully, but for want of time and material, nothing further was done with them.

The specific gravity of the oil was very sensibly diminished by the action of the acid mixture. The first determination gave 0.7688, which was not diminished by further treatment, although this value is somewhat higher than the specific gravity of the Pennsylvania distillate, 0.7581. In determining the boiling-point of this product, 50 cc. distilled entirely at 195°–196°, mostly at 196°, under a tension of 760 mm. After purification of a portion of the crude distillate with fuming sulphuric acid, different preparations of the washed and dried oil gave in the hands of different analysts the following percentages of carbon and hydrogen:

I. 0.1508 gram of the oil gave 0.4683 gram CO_2, and 0.2055 gram H_2O.

II. 0.1520 gram of the oil gave 0.4715 gram CO_2, and 0.2109 gram H_2O.

III. 0.1523 gram of the oil gave 0.4733 gram CO_2, and 0.2180 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found. I.	II.	III
C	84.63	84.70	84.61	84.75
H	15.38	15.15	15.42	15.90

The specific gravity of the purified oil was found to be 0.7737 at 20°, and the vapor-density as follows:

0.1421 gram of the oil gave 68.6 cc. of vapor at 182°, under 373.8 mm.

Calculated for $C_{11}H_{22}$.	Found.
5.33	5.43

A determination of its molecular weight by Mr. Hudson gave 158; required for the formula $C_{11}H_{24}$, 156.

In attempting to form the chlorine derivatives of this hydrocarbon, 16 grams of the fraction 196°, Ohio petroleum, the small amount that remained for this experiment, was treated with chlorine until it gained in weight 4.5 grams. After the chlorine product was fractioned four times it collected in very small quantity at 150°–155°. Analysis gave results corresponding to the formula $C_{11}H_{23}Cl$.

I. 0.2042 gram of the substance gave 0.1548 gram AgCl.

II. 0.1938 gram of the oil gave 0.4765 gram CO_2, and 0.2071 gram H_2O.

	Calculated for $C_{11}H_{23}Cl$.	Found. I.	II.
C	69.29	....	69.64
H	12.07	....	11.88
Cl	18.63	18.71	....

Evidently the chlorination had proceeded so far that the monochlorhendecane could not be separated completely from the dichlor derivative, as shown by the high boiling-point, and the large percentage of carbon.

The small amount of the dichlor derivative was not sufficient when purified to give satisfactory analytical data in support of its composition.

Dodecane, $C_{12}H_{26}$, 214°.

Above 193° the fractional separation was continued longer *in vacuo*. At the end of the eighteenth distillation, between 120° and 130°, 1200 grams collected in single degree fractions, for the most part at 122°–124° and 128°–130°.

The latter distilled under atmospheric pressure at 212°–214°, and was therefore selected for the study of the hydrocarbon which according to the corresponding distillate in Pennsylvania oil should be $C_{12}H_{26}$. The crude distillate gave the following percentages of carbon and hydrogen :

	Calculated for $C_{12}H_{24}$.	Found.
C	85.51	85.76
H	14.49	14.55

The specific gravity of this distillate at 20° was 0.7877. 25 grams of the crude distillate was heated with fuming sulphuric acid to 50°, and kept warm on the steam-bath during several hours. Very little sulphurous acid was set free, although the acid became thick and dark. The loss in weight of the oil was 4.5 grams, or 18 per cent. The remaining oil was washed with sodic hydrate and water, and dried over sodium for analysis.

0.1500 gram of the oil gave 0.4650 gram CO_2, and 0.2088 gram H_2O.

	Calculated for $C_{12}H_{26}$.	Found.
C	84.70	84.54
H	15.30	15.47

A determination of its specific gravity at 20° gave 0.7867, with scarcely any change by the action of the fuming acid. Another portion of the crude distillate was shaken with a mixture of nitric and sulphuric acids. The great heat of the reaction was controlled by cooling, and the heavy nitro product allowed to separate by standing. The principal reaction was soon over, the nitro compound separating in needles on standing.

The nitro derivative was readily soluble in hot, but quite insoluble in cold, alcohol. It melted at 165°, and was doubtless a derivative of one of the aromatic hydrocarbons with boiling-points in this vicinity, such as isohexylbenzol, or isoamylbenzol, boiling-points 212°–214°, which are very probably contained in petroleum. After treatment with the acid mixture, the oil was boiled with tin and hydrochloric acid, washed, and boiled with sodium, and then distilled. Its boiling-point was not appreciably changed, but the specific gravity was reduced to 0.7727, a value practically the same as that of the Pennsylvania decane. A determination of its molecular weight by the Beckmann method gave 172; required for $C_{12}H_{26}$, 170.

In forming the chlorine derivatives of this hydrocarbon, 35 grams absorbed 8.5 grams of chlorine, and the product was fractioned under 80 mm. After the tenth distillation about 15 cc. collected at 150°–160°. In this instance, as in one or two others, the distillate taken for chlorination was not purified, and in the distillation the vapors affected the eyes seriously, doubtless on account of substitution in the side chain in the aromatic hydrocarbons contained in the crude distillate. Either on account of decomposition, or want of sufficient material for complete separation, it was not possible to purify this product sufficiently to give satisfactory numbers on analysis, although the results show the formation of a mono- and a dichlordodecane. The amount of chlorine in the distillate 150°–160° came two per cent. too low for monochlordodecane, and no combustion was made. In a higher distillate collected at 190°–200° the following numbers were obtained:

I. 0.2224 gram of the oil gave 0.2607 gram AgCl.

II. 0.1952 gram of the oil gave 0.4411 gram CO_2, and 0.1816 gram H_2O.

	Calculated for $C_{12}H_{24}Cl_2$.	Found. I.	Found. II.
C	60.26	....	61.63
H	10.04	....	10.33
Cl	29.71	28.99	....

While, therefore, the formula of dodecane in Ohio petroleum is not supported by such reliable data as those of the lower constituents, the presence of this hydrocarbon seems to be established beyond question.

The principal constituents of Ohio petroleum have been shown to be identical with those of Pennsylvania petroleum. The higher specific gravity and peculiar qualities of the Ohio distillates depend on the larger proportions of aromatic hydrocarbons, and perhaps of other heavy constituents.

Constituents of Canadian Petroleum from Corniferous Limestone.

In continuing the study of the higher portions of Canadian petroleum, the vacuum-distillates 150°–300°[1] were carried through fifteen additional distillations under 50 mm. As the separations proceeded, the fractions fell 50° or more in boiling-points, large portions collecting below 220°, the point where the separations could be continued without serious decomposition under atmospheric pressure. In single degree fractions after the fifth distillation was continued until the operation had been repeated in all twenty-nine times. As in the other oils, the distillates collected mainly at 159°–161°, 168°–170°, 188°–191°, and 208°–210° (730 mm.) There is even greater necessity in the Canadian than in the Ohio oil that the earlier distillations be carried on *in vacuo*, on account of the greater quantity of sulphur compounds, but more especially, as will be shown in another paper, on account of the greater proportion of unsaturated hydrocarbons and the smaller proportion of the members in question that distil between 160° and 216°. It is, therefore, otherwise impossible to obtain a large proportion of these higher constituents uncontaminated by impurities due to cracking. But the vacuum-distillates are free from the intensely disagreeable odors due to cracking, which are far more pronounced than any to be obtained from Ohio oil. Nevertheless, the natural odor of these compounds, however carefully they have been protected from decomposition before purification, is more pungent than that of those from Ohio oil. Colorless when first distilled, all these distillates become colored on standing, probably on account of polymerism of the unsaturated hydrocarbons alluded to above and of other unstable bodies resembling the terpenes, which are evidently contained in petroleum. That this is the cause of the coloration we have good evidence in the polymerization and the formation of heavier oils in these unsaturated bodies after they have been separated and allowed to stand as long as two years. Furthermore, after these unstable bodies have been removed, the purified oils remain colorless permanently. The higher specific gravity observed in the first vacuum-distillate from Canadian crude petroleum is still retained in the single degree fractions, however long the fractional distillation is continued. But although these portions are heavier than the distillates from Pennsylvania and Ohio oils, they are so much lighter than the naphtenes that the latter bodies cannot be present in any considerable quantity. In general, the ready and abundant formation of nitro derivatives and sulphonic acids is sufficient evidence that the greater specific gravity is due, for the most part at least, to the aromatic constituents. It is quite probable that naphtenes are present in small amounts, and that they are accountable, as has been suggested, for the extreme difficulty in removing the last traces of the less hydrogenized constituents by fuming sulphuric acid, even after vigorous treatment several times repeated. In some instances, nitric and sulphuric acids have given nitro products that have required very long and vigorous boiling with tin and hydrochloric acid for complete reduction, or an equivalent treatment with sodium. Occasionally the reduction with tin and acid has caused the separation of a heavy red oil, insoluble in the acid, and consequently not an amine.

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[1] This JOURNAL, 18, 63.

Decane, $C_{10}H_{22}$, 163°–164°.

The composition of the principal distillates from Canadian petroleum below 150° was found to correspond to what is required by the series C_nH_{2n+2}. Above this point the distillates were small to 158°, but between this point and 162° larger amounts collected and remained persistently at 159°–160° (730 mm.). After treatment with fuming sulphuric acid, a portion of this distillate was still further fractioned until 75 grams distilled at 163°–164° under 760 mm., and with the mercury column all in the vapor. In the crude distillate before treatment with the acid, carbon and hydrogen were determined, with no other purification than drying over sodium. No less efficient means of desiccation removes the water sufficiently for analysis. But since a reddish flocculent precipitate separates when any of these distillates stand with sodium, evidently the percentages of carbon and hydrogen in the crude distillates cannot be accurately expressed by the results of combustion. The precipitation is doubtless caused in part by sulphur compounds which are not wholly removed by alcoholic mercuric chloride, although it is observed when the quantity of sulphur is very small.

0.1610 gram of the oil gave 0.5057 gram CO_2, and 0.1989 gram H_2O.

C	85.67
H	13.72

Before treatment with the acid, a determination of specific gravity at 20° gave 0.7785. After purification with the acid the specific gravity was diminished to 0.7572, nearly the same value as that found in the corresponding fraction of Ohio oil. The penetrating odor of the crude distillate, resembling that of the aromatic hydrocarbons, disappeared entirely after treatment with the fuming acid, and the purified oil gave only the faint characteristic odor of the petroleum hydrocarbons C_nH_{2n+2}. The acid was blackened and gave off much sulphurous acid. 30 grams gave by this treatment 23.4 grams af the purified oil with a loss of 22 per cent. It is interesting to note the higher specific gravity of the unpurified distillate 163°–164° in all these oils—Pennsylvania, Canadian, and Ohio—than that of the higher distillate, 174°. This clearly indicates a larger percentage of mesitylene and perhaps of decanaphtene. The difficulty in removing entirely the heavier body would seem to indicate a trace of the latter.

After the last distillation, the oil was again treated with the fuming acid and dried over sodium for analysis.

0.1723 gram of the oil gave 0.5358 gram CO_2, and 0.2304 gram H_2O.

	Calculated for		
	$C_{10}H_{20}$.	$C_{10}H_{22}$.	Found.
C	85.71	84.51	84.82
H	14.29	15.49	14.85

The oil was again subjected to the action of the acid and analyzed.

0.1561 gram of the oil gave 0.4847 gram CO_2, and 0.2127 gram H_2O.

C	84.67
H	15.14

The slight change in the percentages of carbon and hydrogen evidently shows the presence of a heavy body that is but slowly affected by the acid. This impurity cannot be mesitylene, since this hydrocarbon dissolves readily in the fuming acid. Another portion of the crude distillate was next vigorously agitated with a mixture of nitric and sulphuric acids, allowing the temperature to rise spontaneously nearly to 100°. As soon as the principal action ceased the mixture cooled and an oily nitro body separated, more remaining in solution. After several crystallizations from alcohol, in which it is quite insoluble, the nitro derivative melted at 225°, near the melting-point of trinitromesitylene. The hydrocarbon oil was separated from the acid and boiled several hours with tin and hydrochloric acid, which caused the yellow color to be absorbed by the acid solution, and a small amount of a heavy oil separated, insoluble in the acid, evidently a product of the vigorous reduction. The crude distillate lost 20 per cent. in weight by this purification. The oil remaining after the reduction, when shaken with fuming sulphuric acid, washed, and dried, gave only the characteristic odor of the petroleum hydrocarbons. Upon analysis it gave the following results:

0.1455 gram of the oil gave 0.4517 gram CO_2, and 0.1980 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.67
H	15.49	15.12

While these results point clearly to the composition C_nH_{2n+2} for the principal hydrocarbon with this boiling-point, they also suggest, as has already been mentioned, a constituent of Canadian oil so inert toward reagents that it cannot be removed by ordinary means. No doubt the difficulty is increased by the great dilution of this impurity in the larger body of the decane. In its behavior toward reagents, decanapthene is suggested. Whatever may be the composition of this body, it is doubtless present in largest quantity in Canadian petroleum, a smaller amount in Ohio oil, and a still smaller proportion in Pennsylvania oil. But even in the Canadian oil the proportion is evidently very small.

The formula of the principal constituent at 163° found still further support in a determination of its molecular weight by the method of Beckmann, in which Mr. Hudson obtained 142; the formula $C_{10}H_{22}$ requiring 142.

The purified distillate 160°–161°, Canadian petroleum, behaved toward chlorine precisely like the corresponding distillates from Ohio and Pennsylvania oils. 17 grams absorbed 4 grams chlorine, and was then fractioned *in vacuo*. About 1 cc. was obtained after five distillations at 200°-204°, atmospheric pressure, without decomposition, and it gave by analysis the composition required for $C_{10}H_{21}Cl$:

I. 0.1922 gram of the substance gave 0.1536 gram AgCl.

II. 0.1873 gram of the substance gave 0.4710 gram CO_2, and 0.2070 gram H_2O.

	Calculated for $C_{10}H_{21}Cl$.	Found.	
		I.	II.
C	68.00	....	68.58
H	11.90	....	12.30
Cl	20.11	19.77	....

The quantity of this monochlordecane was too limited to permit of further determinations, as were also the higher portions for the separation of a dichlor derivative sufficiently pure for analysis.

Having at hand a small quantity of the distillate 162°, Berea Grit petroleum, it seemed of interest to ascertain whether it would form a chlorine derivative similar to or identical with those of the oils now under examination. 30 grams of the oil absorbed 8 grams of chlorine in forty-five minutes, and when the product was fractioned it gave a small quantity at 120°-130° with the composition required for $C_{10}H_{21}Cl$.

I. 0.1931 gram of the substance gave 0.1564 gram AgCl.

II. 0.1821 gram of the substance gave 0.4486 gram CO_2, and 0.1871 gram H_2O.

	Calculated for $C_{10}H_{21}Cl$.	Found.	
		I.	II.
C	68.00	....	67.19
H	11.90	....	11.41
Cl	20.11	20.04	....

The formation of this chlordecane confirms the results published in a former paper[1] of this series, showing a hydrocarbon $C_{10}H_{22}$ in Berea Grit petroleum with the boiling-point 162°.

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[1] This JOURNAL, 18, 1.

Decane, 173°-174°.

Above 163° (730 mm.) the absence of single bodies was indicated by the small amounts of distillates to 168°, where the single degree fractions began to increase in quantity. Between this point and 173° nearly 500 grams collected, the greater portion at 169°-171°, which could not be brought closer together without further purification. After drying over sodium, analysis of this distillate gave the following percentages of carbon and hydrogen :

0.1640 gram of the oil gave 0.5151 gram CO_2, and 0.2083 gram H_2O.

C	85.66
H	14.11

A determination of the specific gravity of this distillate at 20° gave 0.7770, a value somewhat higher than the specific gravity of the corresponding Ohio distillate. For the removal of the aromatic hydrocarbons to determine the boiling-point of the principal constituent, all the fractions 168°-173° were agitated and warmed with fuming sulphuric acid, washed, dried, and the distillation continued until after a few repetitions the fractions came together at 169°-170° (730 mm.), or, under 760 mm. and with the mercury column all in the vapor, at 173°-174°. By this treatment the specific graivty was reduced 0.7614, and the percentages of carbon and hydrogen changed in a proportionate degree :

I. 0.1545 gram of the oil gave 0.4810 gram CO_2, and 0.2091 gram H_2O.

II. 0.1446 gram of the oil gave 0.4485 gram CO_2, and 0.1946 gram H_2O.

III. 0.1678 gram of the oil gave 0.5204 gram CO_2, and 0.2246 gram H_2O.

	Calculated for		Found.		
	$C_{10}H_{20}$.	$C_{10}H_{22}$.	I.	II.	III.
C	85.71	84.51	84.90	84.59	84.57
H	14.29	15.49	15.04	14.96	14.89

Although these results indicate the removal of a large portion of the aromatic hydrocarbon, and Analyses II. and III. were made with specimens on which the acid had acted several hours, it is evident that the less hydrogenized body was not even then entirely removed. In further confirmation of the presence still of this constituent, one of the oils treated with the fuming acid was shaken with a mixture of nitric and sulphuric acids. The solution became warm and an oily nitro product separated above the acid. Since Markownikoff preferred purification of the Russian oil with sulphuric acid to avoid the formation of objectionable nitro products, it was inferred that this acid would remove completely the aromatic bodies. But in our experience with American oils, complete purification cannot be reached with the fuming acid alone. At first we relied on decomposition of the nitro product with sodium; but this required long digestions several times repeated, and in Canadian distillates the residual hydrocarbon which contained the nitrogen could not always be entirely removed, as was shown by analysis of a portion of crude distillate purified in this manner:

I. 0.1656 gram of the oil gave 0.5156 gram CO_2, and 0.2241 gram H_2O.

II. 0.1736 gram of the oil gave 0.5419 gram CO_2, and 0.2345 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found. I.	II.
C	84.51	84.90	85.13
H	15.49	15.04	15.01

The specific gravity of this distillate was found to be 0.7618, the same as that purified by fuming sulphuric acid. Another portion of the same crude distillate was treated with the mixture of concentrated nitric and sulphuric acids. The great heat developed was controlled by cooling, and finally the heavy nitro product collected above the acid. 25 grams of the crude distillate lost 9 grams in the formation of the nitro product, equivalent to 36 per cent. In another experiment 25 grams of the crude distillate treated with fuming sulphuric acid lost 6 grams, or 24 per cent. The oil remaining after the first experiment was again treated with the mixture of acids, which caused further separation of the nitro product. For the removal of the nitro compound, the oil was boiled during several hours with tin and hydrochloric acid. The reduction was very slow and a red oil separated, leaving the upper layer colorless. The latter was then agitated with concentrated sulphuric acid, washed, dried, and analyzed :

0.1449 gram of the oil gave 0.4494 gram CO_2, and 0.2051 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found.
C	84.51	84.57
H	15.49	15.73

The oily nitro derivative of the aromatic hydrocarbon deposited crystals on standing, which after recrystallization from hot alcohol, in which it was very sparingly soluble, melted at 169°. The quantity obtained was insufficient for analysis.

The specific gravity of the oil purified as described above was 0.7601, and, as shown by the vigorous means of purification employed, it cannot easily be reduced, although it is materially higher than the specific gravity of the decane 173° separated from Ohio oil, 0.7513, and of the decane from Pennsylvania oil, 0.7467. But the analyses show that the principal constituent is a hydrocarbon of the series $C_n H_{2n+2}$. The molecular weight of this hydrocarbon, determined by the Beckmann method, gave Mr. Hudson 144 ; required by the formula $C_{10}H_{22}$, 142.

In forming the chlorine derivative of this fraction, 35 grams was exposed to the action of chlorine until it had increased in weight 12 grams. After ten distillations *in vacuo*, 5 cc. were collected at 135°–138°, which upon analysis gave values required for $C_{10}H_{21}Cl$:

I. 0.1950 gram of the oil gave 0.4835 gram CO_2, and 0.2143 gram H_2O.

II. 0.2083 gram of the oil gave 0.1672 gram AgCl.

	Calculated for $C_{10}H_{21}Cl$.	Found. I.	II.
C	68.00	67.69	....
H	11.90	12.21	....
Cl	20.11	....	19.86

The crude distillate having been used in the preparation of the chlorine derivatives, the action on the eyes during distillation was severe, doubtless due to substitution in the side chain of the aromatic hydrocarbons contained in the unpurified oil.

In distilling the higher fractions, 5 cc. collected at 170°–180° that distilled under atmospheric pressure at 205°–210°. It was shown by analysis to have the composition required for $C_{10}H_{20}Cl_2$:

I. 0.2405 gram of the substance gave 0.3214 gram AgCl.

II. 0.2059 gram of the substance gave 0.4352 gram CO_2, and 0.1772 gram H_2O.

	Calculated for $C_{10}H_{20}Cl_2$.	Found. I.	II.
C	56.87	....	57.69
H	9.48	....	9.57
Cl	33.65	33.02	....

The specific gravity of this dichlordecane was found to be 1.0484. A determination of its molecular weight by the Beckmann method gave 207; the formula $C_{10}H_{20}Cl_2$ requires 211.

Hydrocarbon, $C_{11}H_{22}$.

Above 173°, the absence of a definite product was shown by the small amount of the distillates to 188°. Especial attention was given to the fractions in the vicinity of 180° with reference to the possibility of a naphtene, since the naphtene $C_{12}H_{24}$ boiling at 180°–185° was separated by Markownikoff from Russian oil, and Pelouze and Cahours found a hydrocarbon $C_n H_{2n+2}$ boiling at 180°–182°, in American (Canadian?) petroleum. But the very small amounts collected within these limits precluded the presence of either of these bodies in any appreciable quantities in Canadian petroleum. The portions distilling between 188° and 200° were gradually brought together at 189°–191°. A portion of the crude distillate was treated with fuming sulphuric acid, and still further fractioned until for the most part it came together at 196°–197° under 760 mm., and with the mercury column all in the vapor. In drying the crude distillate with sodium for analysis the usual reddish flocculent precipitate separated, which doubtless changed somewhat the composition of the oil:

0.1565 gram of the oil gave 0.4921 gram CO_2, and 0.2041 gram H_2O.

C	85.74
H	14.49

This oil gave 0.7889 as its specific gravity at 20°, and, after treatment with ordinary sulphuric acid, 0.7856, the slight difference indicating that this acid has very little action in the cold on this distillate, although the acid was considerably blackened, and sulphurous acid was observed. Another portion of the crude distillate with fuming sulphuric acid developed no heat, and when warmed on the steam-bath the acid was only slightly colored. After this treatment the specific gravity was 0.7832, nearly the same as before. A third portion of the original distillate was agitated with a mixture of concentrated nitric and sulphuric acids. Very little heat was developed, and the mixture was then warmed on the steam-bath. A small amount of nitro product separated as an oil, which crystallized on standing. After crystallization from alcohol, the nitro derivative melted at 150°–154°, near the melting-point of dinitroisodurol, 156°. After heating a long time with sodium, until there was no further action, the specific gravity was found to be 0.7785. The purified oil was submitted again to the same treatment, when its specific gravity was 0.7758. Still another treatment of the same oil with the mixture of the acids and boiling with sodium, also boiling with tin and hydrochloric acid, and agitating with fuming sulphuric acid, reduced the specific gravity only to 0.7729. Analysis I. was made of the oil after the first treatment with the mixture of acids and sodium, and Analysis II. of the oil after the third treatment:

I. 0.1562 gram of the oil gave 0.4901 gram CO_2, and 0.2051 gram H_2O.

II. 0.1628 gram of the oil gave 0.5093 gram CO_2, and 0.2095 gram H_2O.

	Calculated for		Found.	
	$C_{11}H_{24}$.	$C_{11}H_{22}$.	I.	II.
C	84.70	85.71	85.57	85.33
H	15.30	14.29	14.59	14.30

A determination of the molecular weight by the method of Beckmann gave 154; the formula $C_{11}H_{22}$ requires 154.

These results indicate the series C_nH_{2n}, and that the series C_nH_{2n+2} has ceased to represent the principal composition of Canadian petroleum at the boiling-point 196°. But with reference to the series of hydrocarbons that are now recognized as constituting the main body of petroleum, it is not easy to classify this hydrocarbon. It is certainly not an unsaturated member of the ethylene series because it lacks additive power for the halogens, fuming sulphuric acid, etc. Its specific gravity is much less than that of the naphtene that Markownikoff and Oglobine separated at 196°–197° from the Russian oil, 0.8010 at 20°. But it is interesting to observe that the specific gravity of this hydrocarbon is practically the same as Pelouze and Cahours found in the hydrocarbon separated by them at 196°–200° from American petroleum, and which yielded them analytical values, as has already been explained, page 438, corresponding closely to the formula $C_{12}H_{26}$. Since the specific gravity of Pelouze and Cahours is so much larger than that of the crude distillate from Pennsylvania petroleum, 0.7673, it is difficult to escape the conviction that their distillates were prepared from Canadian petroleum, especially since they allude to an examination of oil from Canada, although the source of this particular oil from which were separated the individual hydrocarbons which they described is not evident from their statement.

In studying the constituents of Pennsylvania oil, it was shown that chlorine acts less readily on the principal hydrocarbons than on other constituents. Since this difference in the action of chlorine seemed to afford a means of ascertaining whether Canadian distillates contain any of the series $C_n H_{2n+2}$, a small quantity, 16 grams of the distillate 189°–190° purified with fuming sulphuric acid, remaining after the examination already described, was exposed to the action of chlorine until 3 grams was absorbed, and the product was fractioned *in vacuo* until a small portion, 6 grams, distilled at 189°–190°, atmospheric pressure. This fraction was boiled with sodium to remove, so far as possible, any chlorine derivative remaining, shaken with sulphuric acid, and again distilled. There was finally obtained about 3 grams that gave percentages of carbon and hydrogen agreeing fairly well for $C_{11}H_{24}$. The low values are due to a small amount for chlorine that was not entirely removed by treatment with sodium :

0.1558 gram of the oil gave 0.4803 gram CO_2, and 0.2115 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found.
C	84.70	84.09
H	15.30	15.09

In the formation of chlorine derivatives from the purified fraction 196°, Canadian petroleum, 25 grams absorbed 7 grams chlorine. After five distillations *in vacuo*, 3 cc. collected at 145°–150°, which distilled at 220°–228°, atmospheric pressure, and by analysis gave the values required for $C_{11}H_{21}Cl$:

I. 0 2378 gram of the substance gave 0.1747 gram AgCl.

II. 0.2005 gram of the oil gave 0.5105 gram CO_2, and 0.2097 gram H_2O.

	Calculated for $C_{11}H_{21}Cl$.	Found. I.	II.
C	70.03	....	69.44
H	11.14	....	11.62
Cl	18.83	18.18	....

A determination of the specific gravity of the monochloride at 20° gave 0.8882. With the small quantity of the higher distillates, it was not possible to separate a dichlor derivative in anything like pure condition.

The small amount of the monochloride evidently precluded the possibility of ascertaining with any precision its true boiling-point, and the analysis is chiefly of value in determining the number of carbon atoms in the molecule. The number of carbon atoms received still further confirmation in a determination of the molecular weight by the Beckmann method, which gave 187; the formula $C_{11}H_{21}Cl$ requires 188.5.

Hydrocarbon, $C_{12}H_{24}$.

Above 195° (730 mm.) the distillates were small in quantity to 208°, but between 208° and 212° about 300 grams collected, for the most part at 208°–210°. The specific gravity of the crude distillate was found to be 0.7947, and analysis gave the following percentages of carbon and hydrogen:

0.1554 gram of the oil gave 0.4878 gram CO_2, and 0.1982 gram H_2O.

	Required for C_nH_{2n}.	Found.
C	85.71	85.57
H	14.29	14.18

In order to collect this distillate more closely, a portion of the crude oil was treated with fuming sulphuric acid, washed, dried, and the distillation continued. 37 grams of the oil gave 27 grams after purification. After several distillations it collected at 212°–214° under 745 mm., and with the mercury all within the vapor. Two determinations of specific gravity at 20° gave (I.) 0.7851, and (II.) 0.7857. The carbon and hydrogen were also determined :

0.1586 gram of the oil gave 0.4960 gram CO_2, and 0.2105 gram H_2O.

	Calculated for $C_{12}H_{24}$.	Found. I.
C	85.71	85.27
H	14.29	14.74

These values point to the composition C_nH_{2n} for this constituent of the Canadian oil. In further evidence as to the correctness of this result, another portion of the crude distillate was shaken with a mixture of concentrated nitric and sulphuric acids, the intense heat at first generated controlled, and after the principal action had ceased the solution was kept warm for some time on the steam-bath. An oily nitro product collected above the acid in considerable quantity, but it was not further examined. The hydrocarbon remaining was then agitated with concentrated sulphuric acid, washed with caustic soda, which removed much more of the nitro product from the oil, then with water, and boiled for some time with tin and hydrochloric acid.

The oil remaining was then washed, dried, and warmed during several hours with fuming sulphuric acid, which produced little change, and boiled with sodium. After this purification, analysis still gave values required for a hydrocarbon C_nH_{2n}:

I. 0.1383 gram of the oil gave 0.4332 gram CO_2, and 0.1849 gram H_2O.

II. 0.1406 gram of the oil gave 0.1856 gram H_2O.

	Calculated for $C_{12}H_{24}$.	Found. I.	II.
C	85.71	85.41	Lost
H	14.29	14.86	14.68

In forming the chlorine derivatives of this hydrocarbon, 26.5 grams of the fraction 214°–216° was allowed to absorb chlorine until the weight had increased 9.5 grams, and the product was fractioned eight times *in vacuo*; 5 cc. collected at 160°–170°, which gave, on analysis, the percentage-composition required for $C_{12}H_{23}Cl$.

I. 0.2059 gram of the substance gave 0.1515 gram AgCl.

II. 0.2064 gram of the substance gave 0.5357 gram CO_2, and 0.2128 gram H_2O.

	Calculated for $C_{12}H_{23}Cl$.	Found. I.	II.
C	71.06	....	70.79
H	11.30	....	11.46
Cl	17.53	18.20	....

The specific gravity of this chlorine derivative determined at 20°, was found to be 0.8960. The small quantity of distillate collected within higher limits did not permit of the separation of a dichlor derivative in a pure condition. A chlorine determination gave 27.21; required for $C_{12}H_{22}Cl_2$, 29.95. It formed a thick viscous oil that could scarcely be distilled even *in vacuo* without decomposition. At a temperature slightly higher than that at which this product was collected the distillate was largely decomposed.

The series having been determined by these numbers, the number of carbon atoms was demonstrated by the molecular weight, which was found by the Beckmann method to be 172; the formula $C_{12}H_{24}$ requires 168.

What has been said as to the probability that Pelouze and Cahours worked with Canadian petroleum receives further support in comparing their results on the hydrocarbon they separated boiling at 216°–218° with those described above, although certain important differences appear between their results and mine.

The specific gravity assigned by them to the hydrocarbon 216°–218° was 0.796 at 20°, which is practically the same as the specific gravity of my crude distillate, 0.7947, given above. But their description of the properties of this distillate are not in accordance with my observations. Referring to the action of reagents on their product, they state: "Le brome, l'acide azotique fumant, l'acide sulfurique fumant, ainsi que le mélange de ces deux acides se comportent à son égard comme avec le composé précédent." And after stating, in the description of the preceding compound, that it is not attacked in the cold by bromine, fuming nitric acid, sulphuric acid at the maximum of concentration with nitric acid, nor by fuming sulphuric acid, they state: "Le mélange des acides azotique et sulfurique agit sur le carbure lorsqu'on maintient ces corps pendant quelque temps en ébullition." That this observation does not represent correctly the behavior of this distillate from Pennsylvania, nor Ohio, nor Canadian petroleum, has been clearly shown by experiments described in this paper. It is especially inapplicable to the Canadian distillate, since this oil with a mixture of ordinary concentrated nitric and sulphuric acids, on shaking, immediately develops sufficient heat to raise the temperature to vigorous ebullition of the acid mixture, and to destroy a large portion of the hydrocarbon. In all these experiments the initial reaction had to be controlled by cooling.

Concerning the number of carbon atoms in the hydrocarbon I have separated at this point, it seems to be well established by the molecular weight, $C_{12}H_{24}$, and by the composition of the monochlor derivative, $C_{12}H_{23}Cl$. Yet in a product with a specific gravity much higher than this purified hydrocarbon, Pelouze and Cahours obtained numbers by analysis, as shown above, corresponding closely to the formula $C_{13}H_{26}$, and from the hydrocarbon a chlorine derivative, $C_{13}H_{27}Cl$, also supported by analytical values closely corresponding to the theoretical composition required for this formula.

Summary of Results.

1. That part of Pennsylvania petroleum which boils between 150° and 220° consists chiefly of decane, boiling-point 163°–164°; decane, boiling-point 173°–174°, probably normal decane; hendecane, boiling-point 196°–197°; and dodecane, boiling-point 214°–216°. It contains also in smaller proportions the series of aromatic hydrocarbons boiling within these limits. Allusion has already been made to mesitylene, cumol, pseudocumol, cymol, isocymol, durol, isodurol, and no doubt

others could be identified with sufficient quantities of the petroleum distillates.

2. The composition of Ohio Trenton limestone petroleum within the same limits is represented by the same members of the series C_nH_{2n+2}, and the higher specific gravity of these distillates is caused by a larger proportion of aromatic hydrocarbons.

3. The constituents of Canadian corniferous limestone petroleum from Petrolia, within these limits of temperature, are the same at 163° and 173°. But the hydrocarbons collecting at 196° and 214° have the composition represented by the general formula C_nH_{2n}. Probably a better knowledge of these higher distillates will be gained when the true composition of American petroleum above 220° has been ascertained. The proportion of aromatic hydrocarbons is greater in Canadian than in Ohio petroleum. There are indications in all these petroleums that the heavier constituents include other bodies than the aromatic hydrocarbons, which will require for their identification the manipulation of large quantities of distillates.

General Conclusions.

The results described in this paper make it clear that no conclusions can be arrived at concerning the composition of the principal constituents of American petroleum between 151° and 216° without separating from these bodies the various impurities with which they are contaminated in the crude distillates. However far fractional distillation may be carried, it is impossible to effect a separation of those bodies whose boiling-points do not differ by more than a few degrees. But, fortunately, the principal constituents of petroleum are not affected by reagents under conditions which allow the removal of the contaminating bodies. While the statement of Pelouze and Cahours that the portions of American petroleum under consideration are not affected by nitric acid nor by fuming sulphuric acid, is not supported by the behavior of distillates used by me in this examination, it is true that the principal constituents are not acted upon by those reagents under conditions that permit of purification. A casual examination of the literature of Pennsylvania petroleum is sufficient to reveal the uncertainty and confusion in statements concerning the composition of the portions with higher boiling-points. The principal constituents have more commonly been referred to the series C_nH_{2n+2}, as suggested by Pelouze and Cahours, who included in this series all the petroleum hydrocarbons, even the least volatile oils and paraffin, although on the basis of Warren's investigations allusions have been made to the unsaturated olefine hydrocarbons C_nH_{2n} as constituting the main body of Pennsylvania petroleum above 150°, and the belief has been expressed that the naphtene series C_nH_{2n} would best explain Warren's results. As already stated, above 150° Pelouze and Cahours separated distillates at 162°, 182°, 196°–200°, and 216°–218°, which, with no special purification, gave analytical data corresponding closely to the theoretical values for the series C_nH_{2n+2}. That there are marked differences in the specific gravity of crude and refined distillates appears in the purification of all distillates described in this paper, and it is no easy task to purify the crude distillates so that they shall yield satisfactory analytical data. As shown in the following table, the specific-gravity determinations by Pelouze and Cahours in the products they analyzed are essentially different from those in Pennsylvania distillates herein presented. The percentages of carbon and hydrogen required for the series C_nH_{2n+2} were obtained in fractions whose specific gravity was even higher than that of our crude distillates, which gave values closely agreeing with the series C_nH_{2n}. This difference in specific gravity can only be explained by assuming, which is evidently true, that Pelouze and Cahours overlooked the aromatic hydrocarbons. It does not appear in their reference to American petroleum whether they really operated on distillates from Pennsylvania oil; but on the other hand, their specific-gravity determinations are not widely different from those of distillates from Canadian oil to which occasional reference is made in their publications.

Pennsylvania Petroleum.

Fraction.			Specific gravity.		
Unpurified. C. F. M.	Purified.	P. & C.	C. F. M.	P. & C.	Series.
163°-164°			0.7684 (20°)		$C_n H_{2n}$
	163°-164°		0.7479 (20°)		$C_n H_{2n+2}$
		162°		0.757 (15°)	$C_n H_{2n+2}$
196°-197°			0.7673 (20°)		$C_n H_{2n}$
	196°-197°		0.7581 (20°)		$C_n H_{2n+2}$
		196°-200°		0.7780	$C_n H_{2n+2}$
214°-216°			0.7745 (20°)		$C_n H_{2n}$
	214°-216°		0.7684 (20°)		$C_n H_{2n+2}$
		216°-218°		0.776	$C_n H_{2n+2}$

Canadian Petroleum.

Fraction unpurified.	Fraction purified.	C. F. M.
163°-164°		0.7785
	163°-164°	0.7582
196°-197°		0.7889
	196°-197°	0.7729
214°-216°		0.7947
	214°-216°	0.7851

If the results of Pelouze and Cahours were readily obtained with distillates from Canadian petroleum, as seems probable, especially since Pennsylvania distillates do not yield such high values, the specific-gravity determinations in the lower distillates agree fairly well with mine in the purified Canadian hydrocarbons.

The results of Warren, on the other hand, are consistent in giving numbers that account both in specific gravity and in percentage-composition for the complex mixture that crude petroleum distillates are known to be. While Warren made no attempt to purify his distillates, they were obtained in a course of fractional separations far exceeding in efficiency those of other experimenters. It is interesting to observe in the following table how clearly the distillates from Pennsylvania petroleum analyzed by Warren resemble in specific gravity the unpurified distillates described in this paper.

Fraction unpurified.	Fraction purified.	Specific gravity.		Series.
		Mabery.	Warren.	
163°-163°		0.7674 (20°)		$C_n H_{2n}$
173°.5		0.7502 (20°)		$C_n H_{2n}$
	173°.5	0.7445 (20°)		$C_n H_{2n+2}$
175°			0.7598 (15°)	$C_n H_{2n}$
196°		0.7673 (20°)		$C_n H_{2n}$
	196°	0.7581 (20°)		$C_n H_{2n+2}$
196°-197°			0.7721 (15°)	$C_n H_{2n}$
216°		0.7745 (20°)		$C_n H_{2n}$
	216°	0.7684 (20°)		$C_n H_{2n+2}$
214°-216°			0.7804 (15°)	$C_n H_{2n}$

Warren found no single body at 162°, his other hydrocarbons correspond in boiling-points with those described in this paper. The series $C_n H_{2n}$ of Warren, with a series of the same numerical composition in Russian oil, led to the suggestion that the naphtenes might form an essential part of Pennsylvania oil. This belief was encouraged by statements that found their way into works on petroleum, that Markownikoff discovered the naphtenes also in Pennsylvania oil. The statement that Markownikoff investigated Pennsylvania petroleum is indeed erroneous,[1] and a closer study shows that the naphtenes cannot be contained in Pennsylvania petroleum in any considerable quantity on account of their higher specific gravity as already shown :

Fraction. unpurified.	Fraction purified.	Specific gravity.		Series.
		Mabery.	Markownikoff.	
163°-164°		0.7684		$C_n H_{2n}$
	163°-164°	0.7479		$C_n H_{2n+2}$
	160°-162°		0.795 (0°)	$C_n H_{2n}$
	180°-185°		0.8119 (0°)	$C_n H_{2n}$
196°-197°		0.7673		$C_n H_{2n}$
	196°-197°	0.7581		$C_n H_{2n+2}$
	196°		0.8055 (14°)	$C_n H_{2n}$
214°-216°		0.7745		$C_n H_{2n}$
	214°-216°	0.7684		$C_n H_{2n+n}$

Even the mixtures that the crude Pennsylvania distillates have proved to be have a much lower specific gravity than those with the same boiling-points from Russian oil. After purification, the Pennsylvania distillates unquestionably have the composition of the series $C_n H_{2n+2}$.

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[1] In a private communication, I am informed by Professor Markownikoff that he has not included Pennsylvania petroleum in his investigations.

Allusion has been made to the great difficulty in removing entirely the constituent with less hydrogen from the distillates prepared for analysis, and also to the fact that, even after the most thorough purification, the specific gravity of the purified distillate is appreciably higher than that of the hydrocarbon with the same boiling-point prepared by synthetic methods. These facts may indicate the presence in small quantity of naphtenes which are acted on only very slowly by reagents, especially when largely diluted in the main body of the principal constituent.

Structure of the Petroleum Hydrocarbons, 160°–216°.

In comparing the petroleum hydrocarbons with the corresponding bodies synthetically prepared, it is but fair to state that the literature of the latter is not altogether satisfactory. The properties of normal decane as it was prepared by Lachowicz,[1] by the action of sodium on a mixture of normal octyl bromide and ethyl iodide, and also by Krafft,[2] by heating caprinic acid with a mixture of hydriodic acid and phosphoric pentachloride, seem to define the corresponding petroleum hydrocarbon as the normal compound.

The boiling-point of the hydrocarbon synthetically prepared is 173° under 760 mm., and the specific gravity 0.7456 at 0°. The boiling-point assigned by me to petroleum decane is 173°.5, and its specific gravity at 20° is (from Pennsylvania petroleum) 0.7486. Evidently the decane obtained by Thorpe and Young by heating solid paraffin, boiling at 166°–168°, specific gravity 0.7394 at 13°.5, is an impure normal hydrocarbon.

A decane has been obtained by several methods, boiling at various temperatures between 157° and 162°. Active diamyl boiling at 159°–162°, specific gravity 0.7463 at 22°, with a high dextro rotatory power, was obtained by Just, on treating active amyl iodide with sodium. But the petroleum decane has not the same form, since it shows no influence on polarized light. The latter has with greater probability the same form as diisoamyl, obtained by Würtz on heating isoamyl iodide with sodium. The boiling-point of this secondary decane is given by Würtz as 158°, with no mention of barometric tension, and its specific gravity as 0.7413. Petroleum decane boils at 163°, and its specific gravity at 20° is 0.7479. In a similar reaction using amyl bromide, Grimshaw[1] obtained a decane boiling at 168°, under 751 mm. Either the normal bromide must have been used in this reaction giving normal decane, or the boiling-point of the product is too high.

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[1] Ann. Chem. (Liebig), **220**, 179. [2] Ber. d. chem. Ges., **15**, 1695.

Normal hendecane (or undecane) was prepared by Krafft[2] from the aldehyde rautenol by the same reaction that he used for decane. Its boiling-point is given as 194°.5 under 760 mm., and the specific gravity as 0.7411 at 20°. Since the boiling-point, 196°–197°, and specific gravity, 0.7581, of petroleum hendecane and the formula of this body, $C_{11}H_{24}$, determined by its molecular weight, corresponded so closely to normal hendecane, it has doubtless the same form. As already explained, the higher specific gravity may be due to a small proportion of a naphtene.

The formula $C_{12}H_{26}$, which represents the petroleum hydrocarbon boiling at 214°–216°, is supported by that of normal dodecane which Krafft[3] obtained by the reduction of laurinic acid. Normal dodecane boils at 214°.5, atmospheric pressure, and its specific gravity at 20° is 0.7511. The specific gravity of petroleum dodecane was found to be 0.7729.

Relation between Specific Gravity and Chemical Composition of Petroleum Distillates.

One interesting result of the examinations described in this paper, and other papers of this series, is the relation between the chemical composition of the individual hydrocarbons and the density of the crude oils from which they were prepared. Pennsylvania petroleum with the lowest specific gravity, 0.80–0.82, is composed below 220° of the hydrocarbons C_nH_{2n+2}. Ohio oil, next higher in the scale of specific gravity, 0.82–0.85, still contains below 220°, as its principal constituents, hydrocarbons of the same series. As the density increases in the Canadian oil, specific gravity 0.85–0.88, the series C_nH_{2n+2} represents the principal constituents up to and including decane, boiling-point 173°, the higher members having the composition C_nH_{2n}. Both oils with higher specific gravity, such as South American petroleum, specific gravity 0.9486, described in another paper of this series, contain only hydrocarbons of the series C_nH_{2n}, and in Caucasus petroleum, specific gravity 0.88, Markownikoff and Oglobine found as the principal constituents the naphtenes, series C_nH_{2n}.

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[1] Ber. d. chem. Ges., **10**, 1602.

[2] *Ibid.*, **10**, 1697.

[3] *Loc. cit.*, 1698.

Action of Sulphuric Acid on Petroleum Distillates.

Since the beginning of the petroleum industry, the sole method of refining has depended on agitation with sulphuric acid; yet, notwithstanding the large quantities of material that sulphuric acid removes, as shown by the immense sludge heaps in the vicinity of the refineries, the refiner has not the slightest notion as to what the acid accomplishes beyond his principal object, which is to prepare acceptable products for the market. Neither has any scientific study been made of this problem, at least in American petroleum, so far as revealed by published statements; but that this is an interesting as well as a difficult subject appears from results described in several papers of this series. That ordinary concentrated sulphuric acid has some effect on the density of petroleum distillates is evident from numerous experiments described in this paper. But without independent evidence, it cannot be determined just what constituents are affected by the acid. That some of these constituents, present in small quantity, are unstable and easily acted on by reagents is evident. The refiner must avoid an elevation of temperature during treatment with the acid, otherwise a color appears in the oil that is difficult to remove without redistillation. Evidently an increase in temperature permits of troublesome chemical changes between the acid and the oil, with the formation of products that remain in solution. The skillful refiner is also careful to remove the acid by washing before adding caustic soda to avoid an objectionable color.

In studying the action of sulphuric acid on different distillates from the Russian oil, Markonikoff and Oglobine[1] attributed the influence of the acid mainly to its action on the unsaturated hydrocarbons and the oxygen compounds. Having separated a series of unsaturated hydrocarbons from Canadian petroleum (Mabery and Quayle, unpublished results), and having ascertained the presence of the same bodies in Ohio petroleum,[2] on account of their unstable character and the ease with which they polymerize alone, or more readily when in combination with sulphuric acid, we are convinced that one important office of the acid is the removal of these compounds. With reference to the oxygen compounds in American petroleum, they seem to collect, for the most part at least, in the distillates above 225°. In the composition of their unpurified distillates Markonikoff and Oglobine found a considerable difference between the total percentages of carbon and hydrogen and 100 per cent., which they assigned to oxygen. In analysis of unpurified distillates described in this paper, the total percentages of carbon and hydrogen in most instances have approached 100 per cent. to within the limit of the error of analysis, although it is true that these distillates were subjected to close fractional distillation within 1°, while those of Markownikoff and Oglobine were distilled only a few times within limits of 5°. In all the distillations of Pennsylvania, Ohio, and Canadian petroleum, a slight coloration of the still-residue after a long series has been observed, which may be caused by a small amount of oxygen compounds.

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[1] Ann. chim. phys. (6), **2**, 404.

On standing with metallic sodium, all the unpurified distillates described in this paper deposit flocculent precipitates, more or less colored, which are evidently products of decomposition. This cannot be due to the action on the principal hydrocarbon, since, when purified, such action by sodium is not observed. Neither should the aromatic hydrocarbons behave in this manner toward sodium. These precipitates must be formed from the oxygen or the nitrogen compounds in the oils, probably from the former. They cannot be due to decomposition of sulphur compounds, since Pennsylvania oil contains only a very small percentage of sulphur, and the other distillates were all treated with alcoholic mercuric chloride. It is quite probable that ordinary sulphuric acid combines to a certain extent with some of the aromatic hydrocarbons. A more extended study of the action of sulphuric acid on a larger scale as in refining, would doubtless be interesting and profitable.

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[2] This JOURNAL., 13, 5.

Concerning the action of fuming sulphuric acid, no further explanation is necessary than has been given in connection with the experiments which describe its behavior toward these petroleum distillates.

So far as possible, all details of this work have been carried on under my immediate and constant personal supervision. For efficient aid I am indebted to the following gentlemen: Messrs. C. A. Soch, private assistant, 1894–95; E. Davidson, 1895-96; E. J. Hudson, molecular-weight determinations, and other aid mainly in connection with the chlorine derivatives of the hydrocarbons; W. F. Priebe, who selected a portion of the work on the Pennsylvania distillates as the subject of a thesis for the degree of Bachelor of Science; and Messrs. Giessen, Watson, Worstall, Piwonka, Shaw, and Walker, for faithful assistance in the routine work of distillation and combustions.

The work now in progress includes a study of the pentanes, hexanes, and heptanes in Pennsylvania petroleum, and the composition of the portions of Pennsylvania, Ohio, Canadian, Berea Grit, and South American petroleum between 216° and 350°.

XXVII.—REFRACTIVE POWER OF THE HYDROCARBONS AND CHLORINE DERIVATIVES DESCRIBED IN THE PRECEDING PAPER.[1]

BY CHARLES F. MABERY AND EDWARD J. HUDSON.

Within recent years the refractive power of the hydrocarbons and their derivatives has received considerable attention from Brühl, Thomsen, and others, and attempts have been made to draw conclusions based on the relation between the index of refraction and density, to define structural relations. The experimental data have been obtained for the most part from bodies with a limited number of carbon atoms, in which the differences in refractive power are large. Independently of determinations bearing on theoretical considerations, the refractive power of oils and solutions has been accepted on practical grounds as a valuable property for recognition and for determining degrees of purity.

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[1] Presented to the American Academy of Arts and Sciences, October, 1896.

While it was not to be expected that the determination of refractive power in hydrocarbons with such a large number of carbon atoms as those contained in the higher portions of petroleum would be serviceable in ascertaining the structure of individual hydrocarbons, the wide differences in specific gravity between unpurified and purified distillates led us to believe that similar differences would be observed in refractive power. When subjected to experimental proof, these differences were easily verified.

The determinations of the angle of refraction were made in the latest form of Pulfrich refractometer, made by Carl Zeiss, Jena, and the calculations of the index of refraction by the formula $\mathrm{I} = \sqrt{N^2 - \sin^2 I}$, in which I represents the index of refraction, N the angle of the prism, and I the observed angle. The observations in this refractometer are rapidly made, and the calculations are much simplified by the use of a table arranged by Pulfrich[1] so that from the observed angle the index may read directly from the table.

In the following table giving the refractive power (the excess of the index of refraction over unity), after the numbers representing the refractive power of the distillates purified by a mixture of nitric and sulphuric acids, and with fuming sulphuric acid, the differences between the refractive power before purification and afterwards are given :

	PENNSYLVANIA.		OHIO.		CANADIAN.	
	Ref. power.	Dif.	Ref. power.	Dif.	Ref. power.	Dif.
163°.0						
Unpurified distillate	0.4241		0.4248		0.4276	
After treatment with HNO_3 and H_2SO_4	0.4083	0.0158	0.4123	0.0125	0.4133	0.0143
After treatment with $H_2S_2O_7$	0.4146	0.0095	0.4113	0.0135	0.4127	0.0139
173°.5						
Unpurified distillate	0.4163		0.4239		0.4245	

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[1] Zeit. für Instrumentenkunde, 1888, p. 47.

	Ref. power.	Dif.	Ref. power.	Dif.	Ref. power.	Dif.
After treatment with HNO_3 and H_2SO_4	0.4118	0.0045	0.4134	0.0105	0.4149	0.0096
After treatment with $H_2S_2O_7$	0.4093	0.0070	0.4118	0.0121	0.4138	0.0107
196°.0						
Unpurified distillate	0.4214		0.4251		0.4309	
After treatment with HNO_3 and H_2SO_4	0.4158	0.0056	0.4214	0.0037	0.4219	0.0090
After treatment with $H_2S_2O_7$	0.4163	0.0051	0.4209	0.0042	0.4231	0.0078
216°.0						
Unpurified distillate	0.4249		0.4280		0.4289	
After treatment with HNO_3 and H_2SO_4	0.4209	0.0040	0.4244	0.0036	0.4219	0.0070
After treatment with $H_2S_2O_7$	0.4209	0.0040	0.4241	0.0039	0.4212	0.0077

Inspection of the columns in this table headed Refractive Power shows a gradual increase with the rise in boiling-points, less regular in the unpurified distillates, but more uniform after purification. A comparison of refractive power in the same distillates from all the oils reveals higher values in the Ohio and Canadian distillates than in those from Pennsylvania oil, analogous to the differences in specific gravity referred to in the preceding paper. In the unpurified distillate 163° from all sources, the influence of the large proportions of mesitylene is apparent.

In determining the refractive power of the monochlor and dichlor derivatives of the hydrocarbons between 160° and 216° portions of the product were used whose composition was determined by analysis, as shown in the preceding paper. On account of the limited quantities, purification was not carried as far as would have been desirable, although the proportion of other bodies was probably not sufficient seriously to affect the results. The differences in refractive power between the hydrocarbons and the monochlor derivatives, as well as those between the monochlor and dichlor derivatives are sufficient to demonstrate the influence of the chlorine atoms.

Monochlor derivatives.

Distillate.				Pennsylvania.	Ohio.	Canadian.
125–130	($C_{10}H_{21}Cl$)	from	164°	0.4424		
"	"	"	"		0.4470	
130–140	($C_{10}H_{21}Cl$)	"	174°	0.4445		
"	"	"	"		0.4437	
146–150	($C_{11}H_{23}Cl$)	"	196°	0.4433		
"	"	"	"		0.4457	
"	($C_{11}H_{21}Cl$)	"	"			0.4461
140–145	($C_{12}H_{25}Cl$)	"	216°	0.4456		
"	($C_{12}H_{23}Cl$)	"	"			0.4521
Dichlor derivatives.						
Distillate.						
160–170	($C_{10}H_{20}Cl_2$)	from	164°	0.4639		
"	"	"	"		0.4770	
170–180	($C_{10}H_{20}Cl_2$)	"	174°	0.4604		
"	"	"	"		0.4640	
"	"	"	"			0.4676
190–200	($C_{12}H_{24}Cl_2$)	"	216°		0.4650	
"	($C_{12}H_{22}Cl_2$)	"	"			0.4747

It seems peculiar that the hydrocarbon boiling at 216° obtained from Canadian petroleum, which gives analytical values corresponding to the formula $C_{12}H_{24}$, should have the same boiling-point as the corresponding constituent of Pennsylvania and Ohio oils, and that it should give a chlorine derivative with substantially the same boiling-point. Probably a better understanding of this hydrocarbon will be gained by the study of the higher constituents, which is now in progress.

Contributions from the Sheffield Laboratory of Yale University.

LII.—ON THE MOLECULAR REARRANGEMENT OF THE OXIMES BY MEANS OF CERTAIN METALLIC SALTS.

By William J. Comstock.

The conversion of ordinary benzaldoxime into its stereoisomer was discovered by Beckmann, who effected it first[1] by the action of sulphuric acid, afterwards[2] by the action of hydrochloric acid gas on the ethereal solution. This latter method has since been applied with success to other cases.

The Beckmann rearrangement of an oxime into amide or substituted amide, is effected by means of phosphorus penta-

[1] Ber. d. chem. Ges., **20**, 2766.

[2] *Ibid*, **22**, 433.

chloride,[1] strong sulphuric acid,[2] acetyl chloride[3] and the so-called Beckmann mixture.[4] I have found that several metallic salts are capable of producing the same results. A good example of this is furnished by the behavior of cuprous chloride towards benzantialdoxime. When a cold solution of ordinary benzaldoxime in dry benzene or toluene is treated with cuprous chloride, the chloride dissolves rapidly. If the solution is a concentrated one, the formation of long needles can be noticed at once; if the solution is dilute, the same compound can be precipitated by the addition of petroleum ether. The new compound is an addition-product of two molecules of oxime to one of cuprous chloride, reckoned as CuCl. But instead of being an addition-product of the antioxime, it contains the stereoisomer.

If the benzene or toluene solution is shaken for a few minutes with an excess of cuprous chloride, and the filtered solution heated, a separation of cuprous chloride begins at once. After continued boiling and concentrating the filtered solution, benzamide separates. I have tested the behavior of several oximes, and found in each case that addition-products with cuprous chloride or cuprous bromide could be obtained. This is true of both aldoximes and ketoximes, and in each case the composition of the product was

$$(\text{Oxime})_2 + \text{CuCl or CuBr}.$$

The rearrangement into amide or substituted amide by boiling a solution of the cuprous-halide-oxime, is not, however, a general reaction, and where effected is not necessarily a smooth one. When the solution of cuprous-halide-oxime is heated, there is usually, if not always, to some extent a regeneration of aldehyde or ketone. In some cases the greater part of the oxime is decomposed in this latter way. For instance, on boiling a toluene solution of benzophenoneoxime with cuprous bromide, the greater part was found to be converted into benzophenone.

The tendency of an oxime to form a "molecular compound" with cuprous chloride is so great, that in two cases at least,

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[1] Beckmann, *Ibid*, **19**, 988.

[2] Beckmann, *Ibid*, **20**, 1507.

[3] Victor Meyer and Warrington, *Ibid*, **20**, 500.

[4] *Ibid*, **20**, 2581.

cupric chloride is reduced to *cuprous* chloride. Benzaldoxime and acetoxime are the two compounds whose behavior towards cupric chloride has been studied.

If an aqueous solution of cupric chloride is added to a concentrated aqueous solution of acetoxime, the separation of colorless crystals begins at once, even at low temperature. With very dilute solutions the separation is slower, but the same reaction takes place. These crystals are identical in composition with those formed by the direct action of cuprous chloride on acetoxime dissolved in an anhydrous solvent. As soon as the separation of crystals from the aqueous solution of oxime and cupric chloride begins, the solution shows the presence of nitrous acid by its reaction with potassium iodide solution.

Obviously a portion of the oxime is split into acetone and hydroxylamine, which latter reduces the cupric chloride to cuprous chloride with formation of nitrous acid, while another portion of oxime unites with the cuprous chloride to form the difficultly soluble cuprous-chloride-oxime.

In addition to cuprous chloride and cuprous bromide, antimony trichloride effects the Beckmann rearrangement with the greatest ease. This I have shown in the case of benzophenoneoxime.

As a method of converting an antialdoxime into its stereoisomer, the action of hydrochloric acid on the ethereal solution is obviously simpler than the action of cuprous chloride or cuprous bromide. Nevertheless these changes of the oximes under the influence of metallic salts are not without interest. Whether the action of a metallic salt can lead to the discovery of a missing stereoisomeric oxime when other methods fail, is of course uncertain. No special efforts have been made with this in view, as the group has already been worked up with considerable thoroughness.

In compounds other than oximes, but containing the group —N=C—, the methods of obtaining the two stereoisomeric forms are by no means as satisfactory; and there is no *a priori* reason why, in some of these other cases, a rearrangement should not be effected by the action of metallic salts.

Cuprous chloride, cuprous bromide, and antimony trichloride, all add, with the greatest ease to some of Schiff's bases. A few of these derivatives I shall describe in another paper.

Experimental Part.

Cuprous-chloride-benzsynaldoxime, $(C_6H_5CH=NOH)_2CuCl$.—The best method of preparing this compound is by treating a cold solution of ordinary benzaldoxime in dry toluene with a slight excess of cuprous chloride, shaking gently until no more chloride dissolves. From the filtered solution the cuprous-chloride-oxime can be precipitated by the addition of petroleum ether. The toluene solution can even be warmed gently. On working with weighed quantities it was found that the solution of ordinary benzaldoxime dissolved a little less cuprous chloride than is represented by the above composition. The compound crystallizes in needles which are at first practically colorless, although the solution assumes at once a yellowish-brown color. The crystals become dark on standing in contact with the mother-liquor, and become dark green very quickly when exposed to the air.

The compound has no sharp melting-point. Washed with petroleum ether and dried *in vacuo* it was found to contain 19.1 per cent. of copper. The above composition requires 18.59 per cent. of copper.

By treatment with cold dilute sodium hydroxide solution the copper can be removed and on leading carbonic acid into the filtered solution, benzsynaldoxime separates at once in crystals.

From cupric chloride the compound was obtained as follows: The ordinary oxime was dissolved in alcohol and mixed with an alcoholic solution of cupric chloride; water was then added until the solution became turbid, a drop of hydrochloric acid added, and the mixture kept at ordinary room temperature. The formation of long colorless needles began within a few minutes, but the separation was not complete for several hours. The compound prepared in this way seemed comparatively stable when in contact with the mother-liquor, but showed the same rapid coloration when exposed to the air.

When washed quickly with a small quantity of 50 per cent.

alcohol, and dried *in vacuo*, it gave the following analytical results :

	Found.	Calculated.
Cu	18.8	18.59
Cl	11.7	10.40

Benzsynaldoxime was obtained from this product in the manner described above. The same compound can be obtained by adding ordinary benzaldoxime to a cold solution of cuprous chloride in dilute hydrochloric acid. When the oxime is added to a cold concentrated solution of cuprous chloride in strong hydrochloric acid, a compound crystallizing in small yellow needles is formed. This yellow compound is quite unstable, but it contains the oxime as synoxime (shown as above), and is obviously a double salt, as it is formed only in presence of strong acid. On adding water gradually to this double salt, the formation of the white needles of cuprous-chloride-oxime can be observed.

As to the rearrangement into benzamide, it was carried out in benzene and in toluene solution. The amide was obtained with sharp melting-point after one recrystallization, and was further identified by the formation of ammonia and benzoic acid. The cuprous chloride which separated when this rearrangement was effected, was dirty and mixed with some resinous matter after the solution had been heated for a time, although when the separation first began it was light colored, much lighter than the solution. Benzaldehyde and probably benzonitrile are by-products of the reaction.

I have assumed that the copper separates as cuprous chloride or cuprous bromide in this and similar cases, but have not proved this by analysis.

Cuprous bromide acts like the chloride, but I have not analyzed the intermediate product, which, however, seemed more stable than the cuprous chloride compound.

Other Aldoximes.—Cinnamaldoxime gives with cuprous bromide an addition-product crystallizing from toluene in small yellow needles. For this purpose a mixture of the two stereoisomers[1] was used.

Found Cu = 14.52 ; calculated for $(\text{oxime})_2\text{CuBr}$, Cu = 14.49.

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[1] See Bamberger and Goldschmidt : Ber. d. chem. Ges., **27**, 3428.

It was shown that the Beckmann rearrangement is effected by boiling the toluene solution. The amide of cinnamic acid was not purified, but decomposed by boiling sodium hydroxide solution. Pure cinnamic acid was obtained and identified. Much aldehyde was also formed.

Oenanthaldoxime forms a beautifully crystallized product with cuprous bromide when warmed in ligroïn solution. On cooling the filtered solution the product separates in star-like clusters of long transparent prisms. It proved comparatively stable when exposed to the air; after several hours there was practically no change. The amount of oenanthol regenerated when the toluene solution was boiled seemed large.

Cuprous-chloride-acetoxime, $(C_3H_6NOH)_2CuCl$.—This compound can be prepared in dry benzene, toluene, or ligroïn by the direct action of cuprous chloride. It can be recrystallized advantageously from boiling ligroïn, but undergoes some decomposition on protracted boiling, and changes very quickly on exposure to the air. It crystallizes in colorless transparent plates or inclined prisms, which assume a yellowish color on exposure to the air for a few minutes. The melting-point is not sharp; it softens below 80°, and is completely melted at 96° to a clear fluid of yellowish brown color. On further heating it undergoes energetic decomposition, and has an odor like impure acetamide. The change is, however, essentially a dissociation.

An analysis of the compound crystallized from hot ligroïn gave the following results:

	Found.	Calculated.
Cu	26.17	25.88
Cl	14.61	14.49

The preparation from cupric chloride in aqueous solution has been described in the introduction. An analysis of the compound prepared in this way and dried *in vacuo* without recrystallization gave the following results:

	Found.	Calculated.
Cu	26.70	25.88
Cl	14.83	14.49

On recrystallization from ligroïn the crystals were to the eye exactly like those prepared directly from cuprous chloride.

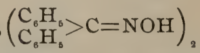
Cuprous-bromide-acetoxime, $(C_3H_6NOH)_2CuBr$. — Preparation as in the case of the previous compound. The bromide is changed less rapidly on exposure to the air and is more difficultly soluble. It melts to a clear fluid at 121°–122°, after softening a few degrees below. It occurs as hexagonal plates or thick, transparent, inclined prisms. A copper estimation gave 22.05 per cent., while the theory requires 21.90 per cent.

The Beckmann rearrangement into methylacetamide could not be effected by boiling the toluene solution of either of these acetoxime derivatives. A solution of the cuprous-bromide-oxime was boiled for hours. The solution became dark colored, and a small quantity of insoluble matter was formed. After boiling off most of the toluene, the entire residue was boiled with strong sodium hydroxide solution, the volatile part being caught in dilute hydrochloric acid. The hydrochloric acid solution left a residue on evaporation, but this residue was not methylamine hydrochloride, as it was not deliquescent and did not give the isonitrile reaction. The distillate from the sodium hydroxide had a distinct bone-oil odor and this same odor was noticed on adding an alkali to the residue from the hydrochloric acid solution. This suggests the formation of a pyridine base, but I did not obtain sufficient for identification.

Other Ketoximes.—Acetophenoneoxime in toluene solution unites with cuprous chloride. The compound was precipitated by ligroïn in thin colorless plates, which darken quickly. Unchanged oxime was recovered after treating with sodium hydroxide solution, filtering and adding carbon dioxide.

Found Cu = 17.7 ; calculated Cu = 17.2.

Boiling in toluene solution led to dark-colored products not carefully examined. Certainly the reaction is not a smooth one.

Benzophenoneoxime and Cuprous Chloride,

$\left(\begin{matrix}C_6H_5\\C_6H_5\end{matrix}>C{=}NOH\right)_2$ CuCl.—This compound was prepared as follows: The oxime was dissolved in methyl alcohol, an excess of cuprous chlo-

ride and a few drops of hydrochloric acid added, the solution warmed on the water-bath to 60° for a few minutes, and filtered from the excess of chloride. On cooling small, thick, yellow plates were deposited. Unchanged oxime could be recovered.

Found, 14.08 per cent.; calculated, 12.86 per cent. copper.

The compound can be obtained in large diamond-shaped, doubly-terminated plates of yellow color, when an excess of cuprous chloride is dissolved, together with the oxime in a mixture of hydrochloric acid, methyl alcohol and chloroform, and the solution evaporated quickly at ordinary temperature. A toluene solution of the oxime boiled in presence of cuprous chloride or cuprous bromide, yielded essentially benzophenone.

Rearrangement with Antimony Trichloride.—When benzophenoneoxime is added in small portions to the antimony trichloride warmed just above its melting-point, the oxime dissolves to a clear solution with but a trace of color. The addition of each portion of oxime produces a hissing sound, and if a large quantity of oxime is added at once, the reaction becomes violent and the product dark-colored.

On slowly adding 1.8 grams of oxime to 6 grams of trichloride, washing the product with a mixture of alcohol and dilute hydrochloric acid and recrystallizing the residue from alcohol, a yield of 1.5 grams of pure benzanilide is obtained.

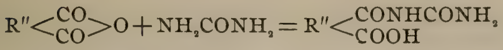
SHEFFIELD CHEMICAL LABORATORY,
NEW HAVEN, MARCH, 1897.

THE ACTION OF UREA AND PRIMARY AMINES ON MALEIC ANHYDRIDE.

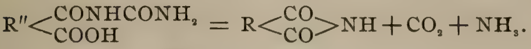
BY FREDERICK L. DUNLAP AND ISAAC K. PHELPS.

In a former article,[1] a method was described by one of us for obtaining imides by the action of urea on the anhydrides of dibasic acids. It was shown that the formation of imides by the interaction of urea and anhydrides was to be explained by the addition of the urea and the anhydrides to form an acid, which when heated, decomposed with the formation of the imide, carbon dioxide and ammonia. These reactions can be shown by the following equations:

[1] This JOURNAL, 18, 332.



$$R''<\begin{matrix}CO\\CO\end{matrix}>O+NH_2CONH_2=R''<\begin{matrix}CONHCONH_2\\COOH\end{matrix}$$



$$R''<\begin{matrix}CONHCONH_2\\COOH\end{matrix}=R<\begin{matrix}CO\\CO\end{matrix}>NH+CO_2+NH_3.$$

In some cases this intermediate product, formed by the addition of the reacting substances, was readily isolated, and upon heating to certain temperatures, it was found that this addition-product decomposed with the formation of the imide.

It was found, in particular, that maleïc anhydride formed an addition-product with urea, and we hoped to obtain the unknown imide of maleïc acid by the decomposition of this addition-product.

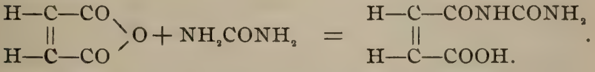
Maleüric Acid.—When equal molecules of maleïc anhydride and urea are heated to 100°–105° in an oil-bath, the mixture melts, and if this temperature is maintained for a short time, the liquid solidifies. This product was purified by crystallization from alcohol, and when pure was perfectly white and melted at 167°.5–168° with decomposition. Upon analysis the following results were obtained :

0.2148 gram substance gave 0.2968 gram CO_2 and 0.0751 gram H_2O.

	Calculated for $C_5H_6O_4N_2$.	Found.
C	37.97	37.69
H	3.80	3.88

Maleüric acid is soluble in hot water and alcohol, fairly insoluble in cold and insoluble in chloroform, benzene, ligroïn, carbon disulphide, acetone, and ether.

Its formation and structure are shown in the following equation :



$$\begin{array}{l}H-C-CO\\ \quad\;\|\\ H-C-CO\end{array}\!\!\!>O+NH_2CONH_2=\begin{array}{l}H-C-CONHCONH_2\\ \quad\;\|\\ H-C-COOH.\end{array}$$

No difficulty was expected in the formation of the imide of maleïc acid, either from the maleüric acid, or by the direct heating of maleïc anhydride and urea ; for, in the cases already studied,[1] the reaction ran with great smoothness and ease. But, for some unknown reason, the imide of maleïc acid could not be obtained—at least in quantities for complete identification. A great many experiments were carried out under varying conditions, but only under one set of conditions could any product be isolated, and then unfortunately the yield was so distressingly small that the study of the compound had to be abandoned. When equal molecules of maleïc anhydride and urea are heated in a boiling-flask, at first slowly, and finally at the full heat of a Bunsen burner, a vigorous evolution of carbon dioxide and ammonia took place, and a small amount of a dark-colored distillate was obtained, which on cooling solidified and gave a melting-point of 130°.5 after crystallation from anhydrous acetone. This same crystalline product was also obtained on distilling the maleüric acid. In both cases a large amount of carbonaceous residue remained in the boiling-flask.

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[1] *Loc. cit.*

Although the method of formation of this compound is exactly parallel to that employed in the preparation of succinimide,[1] yet the identity of this product cannot be regarded as established until sufficient quantities of it have been prepared to subject it to elementary analysis.

The Action of Primary Amines on Maleïc Anhydride.

Anschütz[2] in 1889 published a method by which anilic acids could be very easily prepared by dissolving molecular quantities of aniline and the anhydride of dibasic acids in dry chloroform, when after standing for a short time the anilic acid crystallized out. Following out this line and method of formation, suggested by Anschütz's work, some derivatives of maleïc acid has been prepared and studied.

p-Tolylmaleämic Acid.—Molecular proportions of maleïc anhydride and *p*-toluidine were dissolved in dry chloroform, and upon mixing these two solutions, there immediately separated out a light yellow precipitate. After standing for a time to insure the complete precipitation of the product, it was filtered off and purified by crystallization from alcohol, from which it separated in lemon-yellow needles. The pure product melted at 201°, with evolution of gas. It is readily soluble in ether, acetone and hot alcohol, but insoluble in benzene, ligroïn, carbon disulphide, chloroform and water. Upon analysis the following results were obtained :

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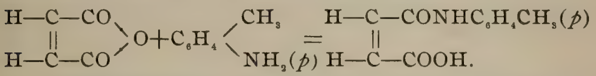
[1] *Loc. cit.*

[2] Ber. d. chem. Ges., **20**, 3214.

0.2072 gram substance gave 0.4881 gram CO_2, and 0.1068 gram H_2O.

	Calculated for $C_{11}H_{11}O_3N$.	Found.
C	64.39	64.24
H	5.37	5.73

The structure and mode of formation of this *p*-tolylmaleämic acid may be seen from the following equation :

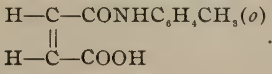


o-Tolylmaleämic Acid.—This acid was prepared similarly to the *p*-tolylmaleämic acid, using molecular proportions of maleïc anhydride and *o*-toluidine. The product was purified by crystallization from alcohol, from which it separated in bunches of thick light yellow prisms. When pure it melted at 117°.5–118°. It is readily soluble in acetone, and in alcohol ; sparingly soluble in chloroform, and insoluble in ligroïn, carbon disulphide, benzene, water, and ether. Analysis gave the following results :

0.2124 gram substance gave 0.4993 gram CO_2, and 0.1146 gram H_2O.

	Calculated for $C_{11}H_{11}O_3N$.	Found.
C	64.39	64.12
H	5.37	5.99

It has the structure represented by the formula



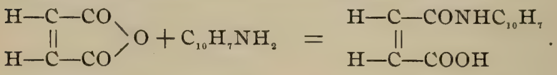
$$\begin{array}{l} H-C-CONHC_6H_4CH_3(o) \\ \quad\;\;\| \\ H-C-COOH \end{array}$$

β-Naphthylmaleämic Acid.—When molecular quantities of *β*-naphthylamine and maleïc anhydride were mixed in dry chloroform solution they reacted and united as readily as did the *o*- and *p*-toluidines and the anhydride. Almost immediately a yellow crystalline precipitate separated out. This, after standing a short time, was filtered off and crystallized from alcohol. It separated from alcohol in small bright yellow needles, which, when pure, melted at 200° with evolution of gas. It is soluble in acetone and alcohol, but insoluble in ether, carbon disulphide, chloroform, benzene, ligroïn, and water. Analysis gave the following results:

0.2033 gram substance gave 0.5226 gram CO_2 and 0.0948 gram H_2O.

	Calculated for $C_{14}H_{11}O_3N$.	Found.
C	69.71	70.11
H	4.56	5.18

This addition-product is obviously formed as follows:



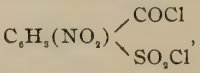
α-Naphthylamine appears also to be added readily to maleïc anhydride, but the product has not been submitted to analysis.

THE KENT CHEMICAL LABORATORY OF YALE UNIVERSITY,
MARCH 8, 1897.

ON THE ISOMERIC CHLORIDES OF *p*-NITRO-*o*-SULPHOBENZOIC ACID.

BY IRA REMSEN AND G. W. GRAY.

The interesting results obtained in the investigation[1] of the chlorides of orthosulphobenzoic acid carried out in this laboratory led to the desire to learn whether a substituted orthosulphobenzoic acid would yield two isomeric chlorides corresponding to those obtained from the unsubstituted acid. As one of the nitro derivatives can be obtained comparatively easily, the action of phosphorus pentachloride upon this was first studied. After a number of obstacles had been overcome, we finally succeeded in finding a method by which it is possible to make both the acid chlorides hoped for, that is to say, the symmetrical chloride of the formula,



$$C_6H_3(NO_2)\begin{cases}COCl\\SO_2Cl\end{cases},$$

and the unsymmetrical of the formula

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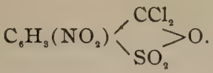
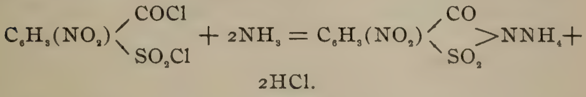
[1] This JOURNAL, **17**, 309, 311, 330, 347; and **18**, 791, 794, 809, 818.



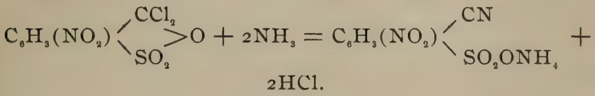
$$C_6H_3(NO_2)\begin{array}{l}\diagup CCl_2\\ \diagdown SO_2\end{array}\!\!>O.$$

Both are well characterized substances, and both undergo characteristic transformations under the influence of various reagents. The symmetrical compound, when treated with ammonia, gives the ammonium salt of the corresponding sulphinide thus:



$$C_6H_3(NO_2)\begin{array}{l}\diagup COCl\\ \diagdown SO_2Cl\end{array} + 2NH_3 = C_6H_3(NO_2)\begin{array}{l}\diagup CO\\ \diagdown SO_2\end{array}\!\!>NNH_4 + 2HCl.$$

While the unsymmetrical compound gives the ammonium salt of the corresponding cyansulphonic acid thus:



$$C_6H_3(NO_2)\begin{array}{l}\diagup CCl_2\\ \diagdown SO_2\end{array}\!\!>O + 2NH_3 = C_6H_3(NO_2)\begin{array}{l}\diagup CN\\ \diagdown SO_2ONH_4\end{array} + 2HCl.$$

Experimental.

The starting-point in the experiments described below was *p*-nitrotoluene. This was treated with fuming sulphuric acid, and thus converted into *p*-nitro-(*o*)-toluene sulphonic acid. The latter was then oxidized with potassium permanganate, and thus changed to *p*-nitro-(*o*)-sulphobenzoic acid, which was easily obtained in the form of the acid potassium salt,

$$C_6H_3\begin{cases}COOH\\ SO_2OK(o).\\ NO_2(p)\end{cases}$$

Action of Phosphorus Pentachloride on the Acid Potassium Salt of Paranitroorthosulphobenzoic Acid.—40 grams of the acid potassium salt are mixed with 60 grams of phosphorus pentachloride, and heated in a distilling-bulb at a temperature of 150°. The distilling-bulb is immersed in a sulphuric-acid bath, and kept at a temperature of 150° for four or five hours. Reaction takes place with the formation of the two chlorides.

The yield of the unsymmetrical chloride appears to be from 80 to 90 per cent. and that of the symmetrical from 10 to 20 per cent. The chlorides must not be heated much above 150°, as decomposition begins at 170°. The yield of the second can be increased to about 30 per cent. by heating in an open dish upon the water-bath. The oily mass is poured into water and washed free from phosphorus oxychloride and potassium chloride. The chlorides are then dissolved in chloroform, and the chloroform solution dried by means of calcium chloride. After filtering off the calcium chloride the solution is allowed to evaporate slowly under a bell-jar free from moist air. From this solution a considerable quantity of the solid (symmetrical) chloride is obtained in crystals which look as if they consisted of monoclinic (?) pinacoids and basal plane. The crystals are filtered off and washed with ice-cold chloroform. After no more crystals can be obtained by this method, more chloroform is added and the solution transferred to an Erlenmeyer flask. This flask is immersed in a freezing-mixture of salt and ice, and dry air drawn over the solution for several days. From this more crystals of the symmetrical chloride, mixed with some of the unsymmetrical, are obtained. These are filtered off and washed very quickly with cold chloroform. This dissolves the unsymmetrical chloride with only a very small quantity of the symmetrical chloride. The chloroform solution was evaporated until all the chloroform had been driven off, and the oil was then dissolved in a large volume of petroleum ether (boiling-point 55°–90°). As the ether solution cools it becomes cloudy and then begins to clear up. When this happens, pour the solution into another beaker and allow the solution to cool. From this solution the unsymmetrical chloride then crystallizes in almost pure condition.

This (unsymmetrical) chloride is slightly soluble in petroleum ether, about 1 part in 200, and from this solvent it crystallizes in fine white needles or long flat plates about 3 to 4 mm. broad and 2 to 3 cm. long. They are extremely soluble in ether and chloroform, but crystals cannot be obtained from these solvents. It is decomposed on heating above 160° and melts at 56°–57° (uncorr.). This chloride is probably identical with that obtained by Kastle.[1]

The symmetrical chloride can be obtained pure by recrystallizing the first crystals obtained above. It can also be obtained by dissolving the two chlorides in chloroform and shaking the solution with dilute ammonia. The ammonia acts immediately upon the unsymmetrical chloride, and only slightly upon the symmetrical. The chloroform solution is washed with water to free it from ammonia, dried by means of calcium chloride, and allowed to evaporate. From the chloroform solution beautiful crystals are obtained, as above described. It is soluble also in ether, but less so than the unsymmetrical chloride. It melts at 94°-95° (uncorr.) It can be heated in a sealed tube at 150° with phosphorus oxychloride without undergoing any decomposition. Both chlorides, when in crystalline form, can be left exposed to moist air without undergoing very much decomposition. When the chlorides are first formed—before crystals are obtained—decomposition goes on more readily, judging by the amount of hydrochloric acid given off.

Portions of both chlorides were heated in a sealed tube with fuming nitric acid. The results obtained were as follows:

0.1933 gram unsymmetrical chloride gave 0.1963 gram AgCl.

0.1933 gram unsymmetrical chloride gave 0.1585 gram $BaSO_4$.

0.1927 gram unsymmetrical chloride gave 0.1950 gram AgCl.

0.1927 gram unsymmetrical chloride gave 0.1548 gram $BaSO_4$.

	Calculated for $C_6H_3\left\{\begin{array}{l} CCl_2 \\ SO_2 \end{array}\right\rangle O. \; NO_2$	Found. I.	II.
Cl	24.97	25.00	25.02
S	11.25	11.28	11.06

The symmetrical chloride on analysis gave:

0.1901 gram symmetrical chloride gave 0.1935 gram AgCl.

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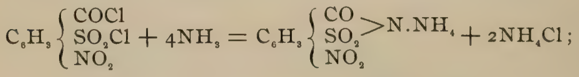
[1] This JOURNAL, 11, 180.

0.1850 gram symmetrical chloride gave 0.1875 gram AgCl.

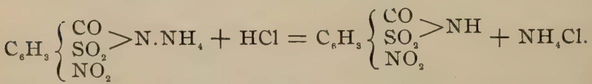
	Calculated for $C_6H_3\left\{\begin{array}{l}COCl\\SO_2Cl.\\NO_2\end{array}\right.$	Found. I.	II.
Cl	24.97	25.15	25.06

Action of Water on the Chlorides.—Cold water acts very slowly upon the chlorides. Even after several months the decomposition is incomplete. In hot water they are not readily decomposed, but, on boiling, the decomposition is complete in a few minutes. The decomposition is about as rapid in one case as in the other. With dilute caustic potash they are readily decomposed, and, after cooling, the addition of an excess of hydrochloric acid causes the appearance of the characteristic acid potassium salt of paranitroorthosulphobenzoic acid from each, thus showing that both yield the same product.

Action of Ammonia upon the Chlorides.—Kastle[1] mentions a product of the action of ammonia upon the chloride, but gives no description of it. It was therefore thought best to repeat this work. Five grams of the symmetrical chloride were dissolved in ether, and poured into a beaker containing 150 cc. of dilute ammonia. The solution was allowed to stand for several days until the ether had evaporated. From this solution the ammonium salt of paranitrobenzoic sulphinide was obtained. The yield is theoretical. The crystals are rectangular plates of glistening flakes, which do not melt below the boiling point of sulphuric acid. It is also soluble in alcohol. On adding hydrochloric acid to this salt paranitrobenzoic sulphinide is obtained. The sulphinide[2] crystallizes in fine needles or plates and melts at 209° (uncorr.).



$$C_6H_3\left\{\begin{array}{l}COCl\\SO_2Cl\\NO_2\end{array}\right. + 4NH_3 = C_6H_3\left\{\begin{array}{l}CO\\SO_2\\NO_2\end{array}\right.\!\!>N.NH_4 + 2NH_4Cl;$$



$$C_6H_3\left\{\begin{array}{l}CO\\SO_2\\NO_2\end{array}\right.\!\!>N.NH_4 + HCl = C_6H_3\left\{\begin{array}{l}CO\\SO_2\\NO_2\end{array}\right.\!\!>NH + NH_4Cl.$$

When the perfectly dry chloride is dissolved in anhydrous ether and dry ammonia gas passed into the solution the same product is obtained.

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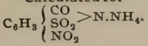
[1] This Journal, II, 181.

[2] Noyes: This Journal, 8, 170.

0.300 gram of this salt gave 0.05147 gram N.
0.300 gram of this salt gave 0.05178 gram N.

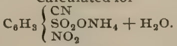
	Calculated for  $C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right. >N.NH_4.$	Found. I.	II.
N	17.18	17.16	17.26

Five grams of the unsymmetrical chloride were dissolved in ether and poured into a beaker containing 100 cc. of dilute ammonia. After the ether had evaporated, nothing crystallized from the solution until it had evaporated to about 50 cc. when a large mass of needles was obtained. These needles grouped themselves in radiating masses or tufts. This product proved to be the ammonium salt of paranitrocyanbenzenesulphonic acid. This salt is also obtained when the mixed chlorides are dissolved in chloroform and shaken with dilute ammonia. From the ammoniacal solution the ammonium salt is obtained on evaporation. From the chloroform solution the symmetrical chloride is obtained.

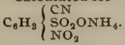
When ammonia is poured upon the unsymmetrical chloride, solution takes place immediately. In the case of the symmetrical chloride solution is not complete even after twenty-four hours.

The analysis of this salt gave the following results:

0.9965 gram lost over sulphuric acid 0.0687 gram H_2O.

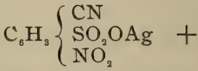
	Calculated for  $C_6H_3\left\{\begin{matrix}CN\\SO_2ONH_4\\NO_2\end{matrix}\right. + H_2O.$	Found.
H_2O	6.85	6.90

0.3000 gram of the anhydrous salt gave 0.05148 gram N.
0.3000 gram of the anhydrous salt gave 0.05196 gram N.

	Calculated for  $C_6H_3\left\{\begin{matrix}CN\\SO_2ONH_4.\\NO_2\end{matrix}\right.$	Found. I.	II.
N	17.18	17.16	17.32

All nitrogen determinations, which are given in grams, were made by the Kjeldahl method, all others by the absolute method. On adding acid to this salt nothing separated out, even on boiling. As further study was desirable in order to place the formation of this salt beyond doubt, a number of salts derived from these two ammonium salts were made. In order to facilitate their comparison the isomeric salts are described under the same heading.

The Silver Salts.

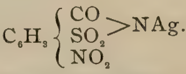
Silver Paranitrocyanbenzenesulphonate,  $C_6H_3\left\{\begin{array}{l}CN\\SO_2OAg\\NO_2\end{array}\right. + H_2O$.—To the hot solution of ammonium paranitrocyanbenzenesulphonate, silver nitrate is added. On cooling, the silver salt crystallizes in fine long rectangular needles 2 cm. long. It contains 1 molecule of water of crystallization, which it loses at 100°.

9.6744 gram of this salt lost 0.0354 gram of H_2O at 100°.

	Calculated for $C_6H_3\left\{\begin{array}{l}CN\\SO_2OAg\\NO_2\end{array}\right. + H_2O$.	Found.
H_2O	5.25	5.10

The anhydrous salt on analysis gave the following results :
0.1779 gram gave 0.0760 gram AgCl.
0.1556 gram gave 0.0667 gram AgCl.
0.2010 gram gave 15.1 cc. N.

	Calculated for $C_6H_3\left\{\begin{array}{l}CN\\SO_2OAg\\NO_2\end{array}\right.$.	Found. I.	II.
Ag	32.21	32.16	32.26
N	8.38	8.63	....

Silver Salt of the Sulphinide,  $C_6H_3\left\{\begin{array}{l}CO\\SO_2\\NO_2\end{array}\right.$ (CO, SO_2 $>NAg$).—This salt was prepared by Noyes[1] by adding silver nitrate to the ammonium salt of the sulphinide. It crystallizes from boiling water (1 part in a 1000) in short fine needles. It is difficultly soluble in boiling water, insoluble in cold. It contains no water of crystallization. It turns brown on exposure to the light.

0.1508 gram gave 0.0645 gram AgCl.
0.1995 gram gave 0.0856 gram AgCl.

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[1] This JOURNAL, 8, 172.

	Calculated for $C_6H_3\left\{\begin{array}{l}CO\\SO_2\\NO_2\end{array}\right.>N.Ag.$	Found. I.	II.
Ag	32.21	32.20	32.30

The Potassium Salts.

Potassium Paranitrocyanbenzenesulphonate, $C_6H_3\left\{\begin{array}{l}CN\\SO_2OK\\NO_2\end{array}\right.+1\frac{1}{2}H_2O$.—This salt is prepared by treating the silver salt with sufficient potassium chloride to precipitate all the silver. The solution is filtered from the silver chloride and evaporated to crystallization. The potassium salt crystallizes in beautiful colorless needles 2 to 3 cm. in length, and contains $1\frac{1}{2}$ molecules of water of crystallization.

9.3177 gram lost 0.0287 gram H_2O at 100°.

	Calculated for $C_6H_3\left\{\begin{array}{l}CN\\SO_2OK\\NO_2\end{array}\right.+1\frac{1}{2}H_2O.$	Found.
H_2O	9.21	9.03

0.1868 gram anhydrous salt gave 9.0605 gram K_2SO_4.
0.2495 gram anhydrous salt gave 0.0802 gram K_2SO_4.

	Calculated for $C_6H_3\left\{\begin{array}{l}CN\\SO_2OK.\\NO_2\end{array}\right.$	Found. I.	II.
K	14.66	14.54	14.43

Potassium Salt of the Sulphinide,[1] $C_6H_3\left\{\begin{array}{l}CO\\SO_2\\NO_2\end{array}\right.>NK$.—This salt was prepared by treating paranitrobenzoic sulphinide with potassium carbonate to neutral reaction. It crystallizes in fine leaflets and contains no water of crystallization. It is easily soluble in hot water, but difficultly soluble in cold.

0.2352 gram of this salt gave 0.0757 gram K_2SO_4.

	Calculated for $C_6H_3\left\{\begin{array}{l}CO\\SO_2\\NO_2\end{array}\right.>NK.$	Found.
K	14.66	14.45

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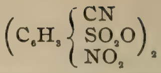
[1] Noyes: *Loc cit.*, 8, 170.

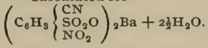
The Barium Salts.



Barium Paranitrocyanbenzenesulphonate, $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right.\right)_2Ba + 2\frac{1}{2}H_2O$.—This salt is made by treating the silver salt with barium chloride. It could not be obtained in well-formed crystals, but formed wart-like masses. It is readily soluble in cold water, and contains $2\frac{1}{2}$ molecules of water of crystallization.

0.3747 gram of this salt lost 0.0265 gram H_2O at 100°.
0.3698 gram of this salt gave 0.1325 gram $BaSO_4$.

Calculated for



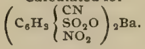
$$\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right.\right)_2Ba + 2\frac{1}{2}H_2O.$$

H_2O	7.07	7.07
Ba	21.08	21.23

It loses $1\frac{1}{2}$ molecules of water of crystallization over sulphuric acid.

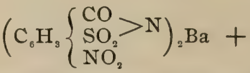
0.2093 gram anhydrous salt gave 0.0822 gram $BaSO_4$.

Calculated for



$$\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right.\right)_2Ba.$$

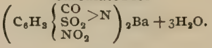
Ba	23.17	23.09



Barium Salt of the Sulphinide,[1] $\left(C_6H_3\left\{\begin{matrix}\left.\begin{matrix}CO\\SO_2\end{matrix}\right>N\\NO_2\end{matrix}\right.\right)_2Ba + 3H_2O$.—This salt is obtained by treating the sulphinide with barium carbonate. The solution is filtered from the excess of barium carbonate and allowed to crystallize. It forms well developed prisms which contain 3 molecules of water of crystallization.

0.3881 gram of this salt lost 0.0329 gram H_2O at 100°.

Calculated for



$$\left(C_6H_3\left\{\begin{matrix}\left.\begin{matrix}CO\\SO_2\end{matrix}\right>N\\NO_2\end{matrix}\right.\right)_2Ba + 3H_2O.$$

		Found.
H_2O	8.37	8.44

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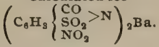
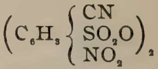
[1] Noyes : This JOURNAL, 8, 171.

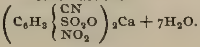
0.3552 gram of the anhydrous salt gave 0.1396 gram $BaSO_4$.

	Calculated for  $\left(C_6H_3\left\{\begin{matrix}CO \\ SO_2 \\ NO_2\end{matrix}\right.\!\!>N\right)_2Ba.$	Found.
Ba	23.17	23.10

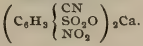
The Calcium Salts.

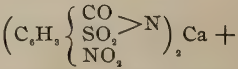
Calcium Paranitrocyanbenzenesulphonate,  $\left(C_6H_3\left\{\begin{matrix}CN \\ SO_2O \\ NO_2\end{matrix}\right.\right)_2$ $Ca + 7H_2O$.—This is formed by treating the silver salt with calcium chloride. It is extremely soluble in water. It is, in fact, soluble in less than its own weight of water. It forms flat elongated plates. It loses 3 molecules of water of crystallization over sulphuric acid and 4 more at 135°.

0.6459 gram lost 0.0543 gram H_2O over sulphuric acid.
0.6459 gram lost 0.1294 gram H_2O at 135°.

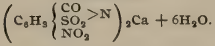
	Calculated for  $\left(C_6H_3\left\{\begin{matrix}CN \\ SO_2O \\ NO_2\end{matrix}\right.\right)_2Ca + 7H_2O.$	Found.
$7H_2O$	20.31	20.04

0.2429 gram anhydrous salt gave 0.0661 gram $CaSO_4$.

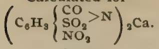
	Calculated for  $\left(C_6H_3\left\{\begin{matrix}CN \\ SO_2O \\ NO_2\end{matrix}\right.\right)_2Ca.$	Found.
Ca	8.09	8.00

Calcium Salt of the Sulphinide,  $\left(C_6H_3\left\{\begin{matrix}CO \\ SO_2 \\ NO_2\end{matrix}\right.\!\!>N\right)_2Ca +$ $6H_2O$.—This is formed by treating paranitrobenzoic sulphinide with calcium carbonate. It forms long, transparent, rectangular columns, which soon lose part of their water of crystallization and become opaque.

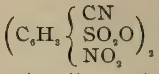
0.7069 gram of this salt lost 0.1272 gram water at 100°.

	Calculated for  $\left(C_6H_3\left\{\begin{matrix}CO \\ SO_2 \\ NO_2\end{matrix}\right.\!\!>N\right)_2Ca + 6H_2O.$	Found.
$6H_2O$	17.93	17.98

0.1013 gram anhydrous salt gave 0.0526 gram $CaSO_4$.

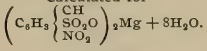
	Calculated for  $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right.>N\right)_2Ca.$	Found.
Ca	8.09	8.09

The Magnesium Salts.

Magnesium Paranitrocyanbenzenesulphonate,  $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right.\right)_2$ $Mg + 8H_2O$.—This salt is formed by treating the silver salt with magnesium chloride. It crystallizes in prisms which are somewhat elongated. It is extremely soluble in water and contains 8 molecules of water of crystallization: of these it loses 3½ molecules over sulphuric acid.

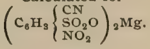
0.3800 gram of this salt lost 0.0494 gram H_2O over sulphuric acid.

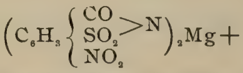
0.3800 gram of this salt lost 0.0882 gram H_2O at 200°.

	Calculated for  $\left(C_6H_3\left\{\begin{matrix}CH\\SO_2O\\NO_2\end{matrix}\right.\right)_2Mg + 8H_2O.$	Found.
3½H_2O	13.01	13.00
8 H_2O	23.12	23.21

0.1695 gram of the anhydrous salt gave 0.0411 gram $Mg_2P_2O_7$.

0.2119 gram of the anhydrous salt gave 0.0493 gram $Mg_2P_2O_7$.

	Calculated for  $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right.\right)_2Mg.$	Found. I.	 II.
Mg	5.09	5.31	5.09

Magnesium Salt of the Sulphinide,  $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right.>N\right)_2Mg +$ 6½H_2O.—This is formed by treating paranitrobenzoic sulphinide with magnesium carbonate. The salt forms beautiful transparent crystals, which seem to be a combination of orthorhombic (?) domes and prisms. These crystals soon lose their lustre and become opaque. The salt contains 6.5 molecules of water of crystallization.

0.2682 gram of this salt lost 0.0527 gram H_2O at 180°.

1.2834 gram of this salt lost 0.2570 gram H_2O at 180°.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right.{>}N\right)_2Mg + 6\frac{1}{2}H_2O$.	Found. I.	II.
$6\frac{1}{2}H_2O$	19.64	19.60	19.97

0.2165 gram of the anhydrous salt gave 0.0523 gram $Mg_2P_2O_7$.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right.{>}N\right)_2Mg$.	Found.
Mg	5.09	5.29

Zinc Salts.

Zinc Paranitrocyanbenzenesulphonate, $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right.\right)_2Zn + 7H_2O$.—This is formed when the silver salt is treated with zinc chloride. It forms long prismatic columns, is extremely soluble in water, and contains 7 molecules of water of crystallization.

0.7453 gram of this salt lost 0.1477 gram H_2O at 170°.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right.\right)_2Zn + 7H_2O$.	Found.
$7H_2O$	19.52	19.82

0.2064 gram anhydrous salt gave 0.0318 gram ZnO.
0.1700 gram anhydrous salt gave 0.0264 gram ZnO.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right.\right)_2Zn$.	Found. I.	II.
Zn	12.60	12.38	12.48

Zinc Salt of the Sulphinide, $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right.{>}N\right)_2Zn + 4\frac{1}{2}H_2O$. —This is formed by treating paranitrobenzoic sulphinide with zinc carbonate. It forms short thick prisms combined with domes, and resembles very much the corresponding magnesium salt. It contains 4.5 molecules of water of crystallization.

0.1861 gram of this salt lost 0.0254 gram H_2O at 125°.
0.4327 gram of this salt lost 0.0593 gram H_2O at 125°.

	Calculated for $\left(C_6H_3\left\{\begin{array}{l}CO\\SO_2\\NO_2\end{array}\right.>N\right)_2Zn+4\frac{1}{2}H_2O$.	Found.	
		I.	II.
$4\frac{1}{2}H_2O$	13.49	13.65	13.71

0.2102 gram of the anhydrous salt gave 0.0328 gram ZnO.

	Calculated for $\left(C_6H_3\left\{\begin{array}{l}CO\\SO_2\\NO_2\end{array}\right.>N\right)_2Zn$.	Found.
Zn	12.60	12.54

The Ethereal Salts.

The Methyl Salt of the Sulphinide, $C_6H_3\left\{\begin{array}{l}CO\\SO_2\\NO_2\end{array}\right.>N.CH_3$.–This salt is formed by heating the silver salt of paranitrobenzoic sulphinide in a sealed tube at 100° with methyl iodide. The methyl salt is extracted with boiling alcohol. On cooling, it crystallizes in leaf-like crystals. It is readily soluble in hot alcohol, but difficultly soluble in cold alcohol. It is also soluble in water. It melts at 179° (uncorr.).

0.1575 gram of this salt gave 14.73 cc. N.

0.1561 gram of this salt gave 14.25 cc. N.

	Calculated for $C_6H_3\left\{\begin{array}{l}CO\\SO_2\\NO_2\end{array}\right.>NCH_3$.	Found.	
		I.	II.
N	11.59	11.77	11.49

From the product of the action of methyl iodide upon the silver salt of paranitrocyanbenzenesulphonic acid nothing definite has been obtained.

The Ethyl Salt of the Sulphinide, $C_6H_3\left\{\begin{array}{l}CO\\SO_2\\NO_2\end{array}\right.>NC_2H_5$. — This salt is formed when the silver salt of the sulphinide is heated in a sealed tube at 100° with ethyl iodide. The mass is extracted with boiling alcohol, filtered, and allowed to cool, when a mass of needles resembling dinitrobenzene is obtained. It is readily soluble in hot alcohol, but difficulty soluble in cold alcohol; it is also soluble in water. It melts at 172° (uncorr.).

0.1509 gram of this salt gave 13.53 cc. N.

0.1645 gram of this salt gave 14.68 cc. N.

	Calculated for $C_6H_3\left\{\begin{array}{l}CO \\ SO_2 \\ NO_2\end{array}\right.\!\!>NC_2H_5.$	Found. I.	II.
N	10.97	11.26	11.21

From the silver salt of paranitrocyanbenzenesulphonic acid we have been unable to obtain an ethereal salt by the action of ethyl iodide, but have obtained a substance which is strongly acid, the nature of which has not yet been determined. It is probably analogous to the orthobenzaminesulphonic acid obtained by Jesurun[1] by the action of alcohol on orthocyanbenzenesulphonic acid.

The reactions are probably those given below:

$$C_6H_3\left\{\begin{array}{l}CN \\ SO_2OAg \\ NO_2\end{array}\right. + C_2H_5I = C_6H_3\left\{\begin{array}{l}CN \\ SO_2OC_2H_5 \\ NO_2\end{array}\right. + AgI.$$

$$C_6H_3\left\{\begin{array}{l}CN \\ SO_2OC_2H_5 \\ NO_2\end{array}\right. + C_2H_5OH + H_2O = C_6H_3\left\{\begin{array}{l}CONH_2 \\ SO_2OH \\ NO_2\end{array}\right. + (C_2H_5)_2O.$$

Paranitrocyanbenzenesulphonic Acid, $C_6H_3\left\{\begin{array}{l}CN \\ SO_2OH \\ NO_2\end{array}\right. + H_2O.$

This acid is formed when its silver salt is treated with enough hydrochloric acid to precipitate all the silver, and also by treating the barium salt with sulphuric acid. The acid crystallizes in long prisms, which contain 1 molecule of water of crystallization. If heated rapidly it melts between 145° and 150°, but solidifies again immediately. This is due to the fact that the acid dissolves in its water of crystallization, and when this is driven off it solidifies. It is soluble in less than its own weight of water. On heating the acid with caustic potash for some time, ammonia is liberated, and then on adding an excess of hydrochloric acid a mass of fine needles resembling the acid potassium salt of paranitroorthosulphobenzoic acid is obtained. When the acid is heated to 130° it loses 1 molecule of water and, if the temperature is then raised to 150°, it begins to increase in weight. This increase is probably due to a change in the cyanogen group.

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[1] Ber. d. chem. Ges.. **26**, 2287.

0.3603 gram of the acid lost 0.0254 gram H_2O at 130°.
0.2503 gram of the acid gave 0.2861 gram N.
0.3033 gram of the acid gave 0.03403 gram N.

	Calculated for $C_6H_3\left\{\begin{array}{l}CN\\SO_2OH + H_2O.\\NO_2\end{array}\right.$	Found. I.	II.
H_2O	7.31	7.06	....
N	11.42	11.43	11.23

Paranitrocyanbenzenesulphone Chloride, $C_6H_3\left\{\begin{array}{l}CN\\SO_2Cl.\\NO_2\end{array}\right.$—The chloride is formed when the potassium salt of paranitrocyanbenzenesulphonic acid is treated with phosphorus pentachloride. One molecule of potassium salt is mixed with one molecule of phosphorus pentachloride, and the mixture heated to 140° in a sulphuric-acid bath for several hours. The mass is then treated with water to decompose the phosphorus oxychloride, and to dissolve the potassium chloride. The chloride is then dissolved in chloroform, and dried by means of calcium chloride. When the chloroform solution is allowed to evaporate, the chloride crystallizes in long rectangular prisms, which melt at 107°–108° (uncorr.). They are soluble in chloroform, ether, and benzene.

0.2640 gram of this chloride gave 0.2538 gram $BaSO_4$.
0.1640 gram of this chloride gave 0.1572 gram $BaSO_4$.
0.2025 gram of this chloride gave 18.75 cc. N.
0.1640 gram of this chloride gave 0.0984 gram AgCl.
0.2640 gram of this chloride gave 0.1544 gram AgCl.
0.1003 gram of this chloride gave 0.0592 gram AgCl.

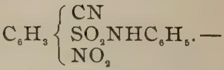
	Calculated for $C_6H_3\left\{\begin{array}{l}CN\\SO_2Cl.\\NO_2\end{array}\right.$	I.	Found. II.	III.
Cl	14.38	14.83	14.46	14.59
N	11.40	11.63	....	....
S	13.00	13.23	13.19	....

Paranitrocyanbenzenesulphonamide, $C_6H_3\left\{\begin{array}{l}CN\\SO_2NH_2.\\NO_2\end{array}\right.$ — The amide is formed when paranitrocyanbenzenesulphone chloride is treated with ammonia. 2 grams of the chloride were dissolved in chloroform and added to an aqueous solution of ammonia. The mixture was shaken in a separating-funnel occasionally. The amide separated as an amorphous mass. This was filtered off and recrystallized from alcohol. It crystallized in small rectangular blocks resembling cane sugar. It does not melt below 270°. The yield is theoretical.

0.1920 gram of this salt gave 28.02 cc. N.

0.1535 gram of this substance gave 22.79 cc. N.

	Calculated for $C_6H_3\left\{\begin{array}{l}CN\\SO_2NH_2.\\NO_2\end{array}\right.$	Found. I.	Found. II.
N	18.33	18.54	18.65

Paranitrocyanbenzenesulphonanilide, 

$C_6H_3\left\{\begin{array}{l}CN\\SO_2NHC_6H_5.\\NO_2\end{array}\right.$—

The anilide is formed in the same way as the amide. Dissolve 1 gram of the chloride in chloroform, and add aniline suspended in water. Heat the solution to drive off the chloroform. As the chloroform is evaporated, the anilide separates as a powder. This powder is recrystallized from alcohol. The yield is theoretical. The anilide crystallizes in fine needles and melts at 207°–208° (uncorr.)

0.1513 gram of this anilide gave 16.97 cc. N.

	Calculated for $C_6H_3\left\{\begin{array}{l}CN\\SO_2NHC_6H_5.\\NO_2\end{array}\right.$	Found.
N	13.94	14.09

The action of aniline and of the toluidines upon the two chlorides was studied to a sufficient extent to show that isomeric anilides and toluides are formed as in the case of the two chlorides of orthosulphobenzoic acid. These products have, however, since been studied more thoroughly by Mr. W. E. Henderson, in this laboratory, and he will publish his results later.

JOHNS HOPKINS UNIVERSITY,
JUNE, 1895.

A STUDY OF FERRIC HYDROXIDE IN PRECIPITATION.

By Vernon J. Hall.

The tendency of many precipitates to carry other substances into precipitation with them is well recognized. Practical illustrations of this are seen in the use of aluminium hydroxide in mordanting and in freeing polluted water of organic matter.

In quantitative analysis it is the cause of much inconvenience, as will be seen from a statement of Fresenius upon the precipitation of ferric hydroxide by an alkali: "If the precipitant alkali is not used in excess, the precipitate contains basic salt; on the other hand, if the alkali has been used in excess, a portion of it is invariably carried down in combination with the ferric hydroxide." In general, it may be said that this tendency is especially characteristic of the metallic hydroxides. However, that it is not limited to gelatinous precipitates is seen in the marked tendency of barium sulphate to carry substances into precipitation, notably barium chloride and iron. In an investigation by A. V. E. Young upon the "Thermo-chemical Reaction between Alum and Potassium Hydrate,"[1] results were obtained which contradicted the theory of cohesion or "mechanical inclusion" as an adequate explanation of this peculiar phenomenon, and warranted a refutation of the equation ordinarily used to represent the true reaction between aluminium sulphate and potassium, hydroxide, *viz.*:

$$Al_2(SO_4)_3 + K_2SO_4 + 6KOH = 4K_2SO_4 + Al_2(OH)_6.$$

For the purpose of ascertaining if these same facts are true concerning other precipitates closely related in nature to aluminium hydroxide, I have studied the precipitation of ferric hydroxide with reference to its effect upon potassium sulphate. The reaction studied is ordinarily expressed by the following equation:

$$Fe_2Cl_6 + 6KOH + 4K_2SO_4 = Fe_2(OH)_6 + 6KCl + 4K_2SO_4.$$

The results of the work will show that this equation does not completely represent the reaction. As in the case of aluminium they show the "mechanical inclusion" theory inadequate, and point toward a phenomenon of a strictly chemical nature.

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[1] This Journal, 8, 23.

Solutions.

I made the solutions for the work as follows:

(1) A dilute solution of potassium hydroxide standardized by titration against oxalic acid as well as gravimetrically.

(2) A dilute solution of sulphuric acid standardized by titration against the potassium hydroxide solution. It was very important that the exact content of these solutions should be known, so, in addition to the titrations, I made gravimetric determinations of the potassium sulphate introduced into each system.

(3) A solution of ferric chloride made by dissolving 11.2 grams of pure iron wire in hydrochloric acid, evaporating the excess, oxidizing with nitric acid, and making up to a liter with water (Temperature 18½° C.). Care was taken that all the nitric acid was expelled, as the determination of barium sulphate in the presence of even small quantities of nitric acid is unsatisfactory.

General Method.

Since washing changes the composition of the precipitate, I analyzed the filtrates, and subtracted the quantities of each constituent found from the total introduced. This method has been followed throughout the work.

Series I.

The first point to be determined was whether or not sulphur trioxide or potassium oxide were carried down when potassium hydroxide was added in the proportion of six molecules. With this in view I made up a system as follows: Into a 500 cc. flask, the same used throughout the work in all volumetric measurements, I introduced sulphuric acid and then exactly neutralized this with potassium hydroxide, making a quantity of potassium sulphate equivalent to four molecules. To this I added 50 cc. of ferric chloride solution; then potassium hydroxide, equivalent to six molecules; and finally enough more to neutralize the free acid of the ferric chloride solution. The quantity necessary for this was determined as follows: To 50 cc. of the ferric chloride solution I added potassium hydroxide to alkaline reaction, using phenolphthaleïn as an indicator. This gave the total acid in the solution. Knowing the quantity of the iron in 50 cc., I calculated how much potassium hydroxide was needed to be in the proportion of six molecules to one of ferric chloride. This quantity, subtracted from that necessary for alkaline reaction, gave the quantity equivalent to the free acid in the ferric chloride solution.

The system already constituted according to the equation before indicated, was made up to 500 cc. with water (Temperature 18½° C.). Of this mixture, well stirred, I drew off 200 cc. into the original 500 cc. flask, dissolved the precipitate by hydrochloric acid, and reprecipitated, while warm, with ammonium hydroxide.

After boiling vigorously for fifteen or twenty minutes with an excess of ammonium hydroxide present, the mixture was cooled and made up to 500 cc. (Temperature 18½° C.). It was then thrown upon a dry filter, received into a dry flask and labeled "Total" for subsequent determination of total sulphur trioxide and potassium oxide in the system. I assumed that this operation liberated any sulphur trioxide and potassium oxide carried down in the first precipitation of ferric hydroxide. That this assumption is true is shown by the constancy of the values for "Totals" in the several systems made up, and still more conclusively by the blank experiments. The latter were made by constituting a system without ferric chloride, but with the same quantities of sulphuric acid and potassium present as in the system already described, and following exactly the same procedure. The following is a comparison of the results:

Mean of twenty-six determinations of sulphur trioxide on "Totals" of twelve different systems, 0.1161 grams per 50 cc. of solution.

Mean of two determinations made on "blanks" in Series I, Experiment 3, 0.1166 gram per 50 cc. of solution. The difference 0.0005 amounts to less than 0.5 per cent. of the quantities measured.

Table—Series I.

Experiment.	Mol. KOH.	Fe_2O_3 in total.	Fe_2O_3 in filtrate.	Fe_2O_3 in precipitate	SO_3 in total		SO_3 in filtrate.		SO_3 in precipitate.	K_2O in total.		K_2O in filtrate.		K_2O in precipitate.	Per cent. total Fe_2O_3 in precipitate.		Per cent. total SO_3 in precipitate		Per cent. total K_2O in precipitate.
1	8	.0800	.0000	.0800	.1169 .1167	.1168	.1178 .1179	.1179	.0000	.3334		.3311		.0023	100.00		0.00		0.69
2	8	.0800	.0000	.0800	.1164 .1159	.1161	.1169 .1175	.1172	.0000	.3338 .3329	.3333	.3305 .3305	.3305	.0028	100.00		0.00		0 84
3	6	.0800	.0000	.0800	.1166* .1166* .1162 .1161	.1164	.1168 .1167 .1176 .1172	.1170	.0000	.2884* .2879* .2875 .2883	.2880	.2867 .2865	.2866	.0014	100.00		0.00		0.48
4	5	.0800	.0009	.0791	.1164 .1161	.1163	.1036 .1037	.1037	.0126	.2629		.2640 .2635	.2638	.0000	98.8	98.9	10.8	11.0	0.00
5	5	.0800	.0007	.0793	.1169 .1173	.1171	.1040 .1038	.1039	.0132	.2631 .2621	.2626	.2650 .2640	.2645	.0000	99.1		11.2		0.00
6	4	.0800	.0108	.0692	.1168 .1176	.1172	.1027 .1030	.1029	.0143	.2396 .2396	.2396	.2404 .2407	.2406	.0000	86.4	84.3	12.2	11.5	0.00
7	4	.0800	.0146	.0654	.1159 .1162 .1158	.1159	.1033 .1030	.1032	.0127	.2399 .2405	.2402	.2401 .2399	.2400	.0000	81.8		10.9		0.00
8	3	.0800	.0308	.0492	.1167 .1167 .1160	.1165	.1055 .1054 .1052	.1054	.0111	.2158 .2156	.2157	.2164 .2164	.2164	.0000	61.5		9.53		0 00
9	2	.0800	.0511	.0289	.1164 .1165	.1165	.1097 .1094	.1096	.0069	.1929 .1923	.1926	.1923 .1932	.1928	.0000	36.1		5.92		0.00
10	8	.1600	.0000	.1600	.1161 .1160	.1161	.1165 .1163	.1164	.0000	.5229 .5225	.5227	.5169 .5175	.5172	.0055	100.00		0.00		1.05
11	5	.1600	.0012	.1587	.1168 .1159	.1163	.0852 .0854	.0853	.0310	.3911		.3944		.0000	99.2		26.6		0.00
12	4	.1600	.0335	.1265	.1159 .1153	.1156	.0881 .0878	.0880	.0276	.3449		.3460		.0000	79.0		23.9		0.00

* Blanks.

Mean of two determinations of potassium oxide made in Series I, Experiment 3, 0.2879 gram per 50 cc. of solution.

Mean of two determinations made on "blanks" in Series I, Experiment 3, 0.2881 gram per 50 cc. of solution. Here again the difference is inconsiderable, amounting to less than 0.1 per cent. of the quantity measured.

The remainder of the original mixture—solution and precipitate—left in the beaker, was filtered through a dry filter into a dry flask and labeled "Filtrate." Duplicate determinations of sulphur trioxide and potassium oxide were made on this, using 50 cc. for each. The determinations of sulphur trioxide were made according to the ordinary method of precipitating with barium chloride in the presence of free hydrochloric acid and weighing as barium sulphate.

The determinations of potassium oxide were made by evaporating to dryness in a platinum dish with a slight excess of sulphuric acid present, expelling the excess, and igniting the potassium sulphate to constant weight.

Of the "Total" solution, 100 cc. were used for each determination. These were also made in duplicate and in the same manner as in the case of the "Filtrate" solution. It is to be seen that by using 100 cc. of the "Total" for each determination, I obtained results for barium sulphate, which multiplied by 12.5 and divided by 10 became comparable with the quantities in the "Filtrate."

Were the reaction between ferric chloride and potassium hydroxide completely represented by the equation before given, I should obtain the same quantities of sulphur trioxide and potassium oxide in the "Filtrate" as in the "Total," for the potassium sulphate is supposed to take no part whatever in the reaction. The results in Series I, Experiment 3, show that this is not true. They are as follows:

$$\begin{array}{lcl} K_2O \text{ in ``Total''} & = & 0.2880 \pm 0.0003 \\ K_2O \text{ in ``Filtrate''} & = & \underline{0.2866} \pm \underline{0.0001} \\ K_2O \text{ in precipitate} & = & 0.0014 \pm 0.0004 \end{array}$$

$$\begin{array}{lcl} SO_3 \text{ in ``Total''} & = & 0.1164 \\ SO_3 \text{ in ``Filtrate''} & = & \underline{0.1170} \\ SO_3 \text{ in precipitate} & = & 0.0006 \end{array}$$

These results show unmistakably that sulphur trioxide is absent, but that about 0.5 per cent. of the total potassium oxide in the system is present in the precipitate. The quantity is very small as a basis for conclusion, but an examination of the data shows that the probable error is only ± 0.0004.

Using the same quantities of potassium sulphate and ferric chloride as before, I proceeded to precipitate the ferric chloride with five molecules of potassium hydroxide and note the change, if any, in the composition of the ferric hydroxide precipitate. After shaking thoroughly, I made up the mixture to 500 cc. with water (Temperature 18½° C.). The "Totals" were made as before. The "Filtrates" were made as follows: After the ferric hydroxide had been filtered out, I drew off 200 cc. of the filtrate into the 500 cc. flask, boiled with ammonium hydroxide, cooled and made up to volume (Temperature 18½° C.). The ferric hydroxide was then filtered out and determined, and the filtrate received into a dry flask. The need of this slight variation in the method of preparing the "Filtrate" arises from the fact that at five molecules the iron is not completely precipitated, and the remainder must be removed before sulphur trioxide can be determined successfully. It is to be noted, however, that at five molecules the precipitation is very nearly complete, the quantities found in the filtrate being about 1 per cent. of the total quantity of ferric oxide introduced into the system.

A marked change in the composition of the precipitate at this point, as compared with that of six molecules, is to be noted. While at six molecules the sulphur trioxide was undisturbed, and potassium oxide was carried down, on the contrary, at five molecules, 11 per cent. of the total sulphur trioxide present is carried into the precipitate and potassium oxide is undisturbed.

In a subsequent series of experiments I used the same quantities of potassium sulphate and ferric chloride, again only partly precipitating the ferric hydroxide with four, three and two molecules successively. The "Totals" and "Filtrates" were made in the same manner as at five molecules. The results were given in Series I, Experiments 6, 7, 8 and 9. They show a regular decrease in the quantity of sulphur trioxide in the precipitate, although an increase in proportion to the ferric hydroxide in the same. The differences, however, in the quantities of sulphur trioxide at five and four molecules were so small, and so closely approached the limit of error as to make it uncertain whether these differences were real. I therefore increased the magnitude of the phenomenon by using twice as much ferric chloride and potassium hydroxide, but the same quantity of potassium sulphate. The results, Experiments 11 and 12, show unmistakably a decrease in sulphur trioxide in passing from five to four molecules of potassium hydroxide. They show further that by increasing the ferric hydroxide in the system 100 per cent., the sulphur trioxide is increased 100 per cent. or more.

In addition to the experiments just mentioned, I made two others, using eight molecules of potassium hydroxide. For the results see Experiments 1 and 2. They show the absence of sulphur trioxide and an increase of about 100 per cent. of potassium oxide in the precipitate over that at six molecules. These also are verified by a third in which the phenomenon was increased as just mentioned (See Experiment 10). This again shows that increasing the ferric hydroxide in the system greatly increases the potassium oxide present in the precipitate.

Upon completing the work just described I proceeded to investigate the action of ferric hydroxide upon substances other than potassium sulphate. The following question presented itself for consideration: What will be the action of ferric hydroxide upon potassium chloride, in the system constituted according to the following equation:

$$Fe_2Cl_6 + 6KOH = Fe_2(OH)_6 + 6KCl \ (?)$$

To answer this question, I introduced into systems, each containing a constant quantity of ferric chloride, potassium hydroxide in varying molecular proportions, and, as outlined in the previous work, determined the action of ferric hydroxide upon potassium chloride by differences between "Totals" and "Filtrates." Owing to the fact that chlorine cannot be determined as silver chloride in the presence of ammonium salts, I could not remove the iron by ammonium hydroxide from the "Totals" and "Filtrates" at points of incomplete precipitation as I have uniformly done heretofore. It was necessary therefore to determine the chlorine in the presence of iron. Whether or not this could be done successfully was the first point considered. For this purpose I made up a solution containing a quantity of chlorine approximately equivalent to the chlorine in the ferric chloride solution. Of this solution I drew off two portions of 50 cc. each for determinations of total chlorine introduced. Also two other portions of 50 cc. each of which I treated as follows: To one portion I added a quantity of iron in the form of a solution of ammonium iron alum, approximately equal to that which would be present in the actual determinations. To another portion I added twice this quantity. The chlorine was determined by the ordinary method of precipitation with silver nitrate and weighing as silver chloride. In washing the silver chloride I found it extremely difficult to wash out all the iron, so in addition to the one-tenth gram of silver nitrate, ordinarily used per liter of wash-water, I added twenty-five cc. concentrated nitric acid. I found that this not only removed all traces of iron from the silver chloride, but in addition served to prevent any decomposition of silver nitrate. That the presence of iron in the given conditions does not interfere in the least with the accurate determination of the chlorine as silver chloride, will be seen from the following results:

	No iron.	Containing iron.	
Solution 1	0.4647	0.4640	0.1 gram.
Solution 2	0.4638 0.4637	0.4642	0.2 "
Solution 3	0.4641 0.4636 0.4639 AgCl	0.4637 0.4642 0.4640 AgCl.	0.3 "

Series II.

The first point considered in the investigation was the action of ferric hydroxide upon potassium chloride at complete precipitation of the ferric hydroxide, that is at six molecules.

I made a system as follows: Into a 500 cc. flask I intro-

Table—Series II.

Experiment.	Mol. KOH.	Fe_2O_3 in total.	Fe_2O_3 in filtrate.	Fe_2O_3 in precipitate	Cl in total.		Cl in filtrate.		Cl in precipitate.	Per cent. total Fe_3O_3 in precipitate.		Per cent. total Cl in precipitate	
13	6	.0800	.0000	.0800	.1127 .1127	.1127	.1133 .1133	.1133	.0000	100.00		0.00	
14	6	.0800	.0000	.0800	.1127 .1126	.1127	.1127 .1126	.1127	.0000	100.00		0.00	
15	5½	.0800	.0067	.0733	.1127 .1128	.1128	.1074 .1073	.1074	.0054	91.6		4.79	
16	5	.0800	.0191	.0609	.1132 .1132	.1132	.1081 .1082	.1082	.0050	76.1	76.1	4.42	4.5
17	5	.0800	.0191	.0609	.1127 .1125	.1126	.1074 .1074	.1074	.0052	76.1		4.62	
18	4	.0800	.0479	.0321	.1127 .1125	.1126	.1098 .1098	.1098	.0028	40.1		2.49	
19	3	.0800	.0567	.0233	.1126 .1125	.1126	.1104 .1105	.1105	.0021	29.1		1.87	

duced 50 cc. of ferric chloride solution and then potassium hydroxide in the proportion of six molecules, and enough more to neutralize the excess of acid in the ferric chloride solution. I made this to volume (18½° C.) with water, stirred thoroughly, and drew off three portions of 50 cc. each, containing ferric hydroxide precipitate. In these, after dissolving the precipitate with nitric acid, I determined the total chlorine in the system. The remainder of the mixture was then thrown upon a dry filter and received into a dry flask. Of this I took two portions of 50 cc. each, and determined the chlorine present in the "Filtrate." For results, see Series II, Experiments 13 and 14. They show clearly that no chlorine is present in the precipitate at six molecules, the "Totals" and "Filtrates" being identical.

Using the same quantity of ferric chloride in each as in the experiment just described, I proceeded to constitute systems with five, four and three molecules of potassium hydroxide, and to observe the change, if any, in the composition of the ferric hydroxide. The method followed was identical with that just given for six molecules, with the addition that I made determinations of the ferric hydroxide present in 50 cc. of the "Filtrate" in every case, in order to compare the quantity actually precipitated with that calculated on the basis of the molecular proportion of potassium hydroxide used.

It will be observed that, although the same quantity of ferric chloride is used throughout, less ferric hydroxide is precipitated at five, four and three molecules in these systems than at the corresponding points when potassium sulphate is present in the system. The probable cause for this is that the basic sulphate of iron formed in the system when potassium sulphate is present is less soluble than the corresponding basic chloride formed when potassium sulphate is absent. It will be seen by reference to Series II, Experiments 15, 16, 17, etc., that the same action on the part of ferric hydroxide is maintained toward chlorine as was manifested toward sulphur trioxide when the latter was present in the system in Series I.

At six molecules the chlorine was undisturbed, the "Totals" and "Filtrates" being identical. At points short of complete precipitation of the ferric hydroxide, however—five and one-half, five, four and three molecules—a marked change in the composition of the precipitate is noted. Further it will be observed that the quantity of chlorine present in the precipitate diminishes in going from five and one-half molecules to five, and so on. From this fact it might be inferred that still more chlorine would be found in the precipitate at points beyond five and one-half molecules; in other words, that the maximum quantity of chlorine would be carried down just short of six molecules.

Series III.

In addition to the series just mentioned, I made another, the object of which was to determine whether or not chlorine is disturbed in systems, such as those in Series I, when potassium sulphate is present. These observations were made at six and five molecules. The method of making the solution and the manner of analysis so far as sulphur trioxide is concerned, were identical with those at corresponding points in Series I, except that 1000 cc. of the solution was made up instead of 500 cc. in order to give sufficient material to work upon. In determining chlorine I drew off three portions of 50 cc. each, of solution containing ferric hydroxide precipitate, in which, after dissolving the precipitate with nitric acid, I determined the total chlorine introduced. For the "Filtrate" I drew off 50 cc. portions of the filtered solution. The results of these experiments are shown in Series III, Experiments 20 and 21. At six molecules neither chlorine nor sulphur trioxide appears in the precipitate. At five molecules, however, 13 per cent. of the total sulphur trioxide is carried down and the chlorine is undisturbed. From this it is evident that whenever potassium sulphate is present the ferric hydroxide acts upon it in preference to the potassium chloride.

Discussion.

How far do the results obtained go toward answering the prime question: Is the presence of these substances in the precipitate due to "mechanical inclusion" (occlusion), or to something of the nature of adhesion, or, finally, is it due to chemical action?

Table—Series III.

Experiment.	Mol. KOH.	Fe_2O_3 in total.	Fe_2O_3 in filtrate.	Fe_2O_3 in precipitate	Cl in total.		Cl in filtrate.		Cl in precipitate.	SO_3 in total.		SO_3 in filtrate.		SO_3 in precipitate.	Per cent. total Fe_2O_3 in precipitate.	Per cent. total Cl in precipitate	Per cent. total SO_3 in precipitate
20	6	.0800	.0000	.0800	.1128 .1129	.1129	.1131 .1132	.1132	.0000	.1162 .1161	.1162	.1161 .1156	.1159	.0000	100.00	0.00	0.00
21	5	.0800	.0014	.0786	.1127 .1127	.1127	.1129 .1129	.1129	.0000	.1159 .1151	.1155	.1007 .1004	.1005	.0150	98.2	0.00	13.0
										K_2O		K_2O		K_2O			K_2O
22	6	.2400	.0000	.2400	.3376 .3382	.3379	.3390 .3388	.3389	.0000	.4532		.4512 .4543	.4528	.0000	100.00	0.00	0.00
23	5	.2400	.1112	.1288	.3376 .3378	.3377	.3262 .3262	.3262	.0115	.3773		.3835		.0000	53.7	3.4	0.00

The question may be considered first with respect to sulphur trioxide. In what form has it been carried down? Certainly not as potassium sulphate, as is evident upon a glance at Series I. At six molecules, when potassium oxide appears in the precipitate, sulphur trioxide does not; on the contrary, with five, four, three and two molecules of potassium hydroxide present, sulphur trioxide appears and potassium does not. Were the precipitation made from a solution of ferric sulphate, there might be reason to think that sulphur trioxide appeared in the precipitate as a residue, so to speak, from the ferric sulphate, but the use of ferric chloride instead of ferric sulphate is assumed to remove all such possibility.

It may be claimed, however, that upon mixing ferric chloride and potassium sulphate, ferric sulphate is formed. That the sulphur trioxide in the precipitate is not dependent upon the formation of ferric sulphate, is shown conclusively by R. H. Smith, who varied the experiment by introducing the potassium sulphate after the ferric hydroxide precipitate had been formed, as well as before, and found the quantities carried down in both cases practically the same. A similar fact was shown in the case of aluminium hydroxide. In Series II facts similar to those just discussed for sulphur trioxide were noted in the case of chlorine. At no point were chlorine and potassium carried down at the same time. The proof for this is found in Series III, Experiments 22 and 23. At six molecules neither chlorine nor potassium are disturbed, but at five molecules 3.4 per cent. of the chlorine present appears in the precipitate and potassium is absent. From the preceding discussion it is evident that sulphur trioxide and chlorine can be carried down, in the given conditions, only as a result of the decomposition of potassium sulphate and potassium chloride respectively. This would imply with reference to ferric hydroxide, first, the power of decomposing either potassium sulphate or potassium chloride, as the case may be, and second, the power of selective combination.

Furthermore, this is emphasized by the results in Series III, where chlorine is undisturbed in the presence of potassium sulphate, although carried down when the latter is absent. These facts are certainly inconsistent with the theory of adhesion or "mechanical inclusion," and, on the other hand, are characteristic of chemical action. As to the appearance of potassium in the precipitate at six and eight molecules in Series I, the evidence is not conclusive that it is the result of chemical action, but it suggests the formation of a salt of ferric hydroxide and potassium analogous to potassium aluminate, differing, however, from the latter in that it is insoluble.

CHEMICAL LABORATORY, NORTHWESTERN UNIVERSITY,
EVANSTON, ILL.

REVIEWS.

THE CONSTANTS OF NATURE. Part V. A RECALCULATION OF THE ATOMIC WEIGHTS. By FRANK WIGGLESWORTH CLARKE. Chief Chemist of the U. S. Geological Survey. New edition, revised and enlarged. The Smithsonian Institution. Washington. 1897. pp. 370.

The first edition of this now well known work appeared in 1882. A little later Meyer and Seubert published their book on "Atomic Weights," which was complete up to date. But the activity in the field of atomic weight determinations has been so great recently, that even the *Lehrbuch* of Ostwald, the second edition of which appeared in 1891, is by no means a complete record of what has been done up to the present. The appeareance of this new edition of Clarke's book is therefore timely.

The method which the author adopts in dealing with the results of the different experimenters, together with the reasons for its selection, will be seen best by examining a paragraph from the preface: "That all methods of averaging are open to objections, I am, of course, perfectly aware. I also know the doubts which attach to all questions of probable error, and to all combinations of data which depend upon them. I have, however, preferred to face these objections and to recognize these doubts rather than to adopt any arbitrary scheme which permits of a loose selection of data. After all, the use of probable error as a means of weighting, is but a means of weighting, and perhaps more justifiable than any other method of obtaining the same result. When observations are weighted empirically—that is, by individual judgment—far greater dangers arise. Almost unconsciously, the work of a famous man is given greater weight than that of some obscure chemist, although the latter may ultimately prove to be the best. But the probable error of a series of measurements is not affected by the glamor of great names, and the weight which it assigns to the observations is at least as safe as any other. In the long run, I believe it assigns weight more accurately, and therefore I have trusted to its indications, not as if it were a mathematical fetich, but regarding it as a safe guide, even though sometimes fallible.'' That greater weight should *ceteris paribus* be attached to the use of simple methods than to those which are more complicated, is evident.

Further, that the separate determinations in any one series, made by exactly the same method, should agree with one another, is far less significant than that results by different methods, using different material, should agree. And, what appears to be most significant of all, is that different experimenters, working with different material, and with different methods, should obtain essentially the same result. It is on this ground that we now ascribe to oxygen the atomic weight 15.88, with a good deal of confidence.

But after all, it is but a matter of opinion as to the best method of dealing with results which do not agree closely with one another, in order to obtain the most probable value from them. Indeed, whatever opinion one may hold with respect to the method of assigning final values, this would scarcely affect the standing of this admirable book, for as Clarke states in his preface, ''of course none of the results reached in this revision can be considered as final. Every one of them is liable to repeated corrections. To my mind the real value of the work, great or little, lies in another direction. The data have been brought together and reduced to common standards, and for each series of figures the probable errors have been determined. Thus far, however much my method of combination may be criticised, I feel that my labors will have been useful. The ground is cleared, in a measure, for future experimenters; it is possible to see more distinctly what remains to be done.'' And when we consider the amount and kind of work which has necessarily been spent in calculating upon a common basis all the atomic weight determinations which have ever been made, it is clear that Professor Clarke deserves high praise and the thanks of his brother chemists. H. C. J.

THE CHEMISTRY OF DAIRYING. An outline of the chemical and allied changes which take place in milk, and in the manufacture of butter and cheese; and the rational feeding of dairy stock. BY HARRY SNYDER, B.S., Professor of Agricultural Chemistry, University of Minnesota, and Chemist of the Minnesota Experiment Station. 156 pages. Easton, Pa.: Chemical Publishing Co. 1897.

This little book has been prepared from the author's lecture notes, and is designed for dairy students who have usually no knowledge of chemistry. While necessarily superficial from a chemist's standpoint, the book affords interesting reading for any one who is seeking information in this line. Among the subjects treated are the following: Composition of milk, its products and by-products, milk testing, chemistry of butter and cheese making, sanitary questions of dairy, preserving milk, effects of food upon dairy products.

We notice some statements which do not appear to be in line with present knowledge. Thus, the author, on page 5, appears to confuse caseïn with the total nitrogen compounds. Albumin is used to include all nitrogen compounds exclusive of caseïn. It is stated that the "scum" which forms on boiled milk is albumin, while, in fact, it contains caseïn, sugar and fat as well, and is practically evaporated milk. Another instance is quoting Blyth to the effect that there is a constant ratio between the albumin and caseïn of normal milk. Blyth has been shown to be wrong in this, for the ratio varies greatly. Perhaps such errors in minor details do not detract from the practical value of the book for dairy students. In the main the book can be commended for its accuracy, clearness and comprehensiveness. L. L. V. S.

INORGANIC CHEMICAL PREPARATIONS. BY FRANK HALL THORP, Ph.D., Instructor in Industrial Chemistry, Massachusetts Institute of Technology. Boston: Ginn & Co. 1896.

In the introduction to this book Dr. Thorp describes methods of work and apparatus. The book gives detailed methods for making a large number of salts; the instructions are clear and precise. Nearly all of the preparations are crystallized from aqueous solutions, giving an impression of monotony in the work. By adding to his list of salts some anhydrous halides, such as ferrous bromide and chloride, bismuth iodide, the chlorides of iodine, and some preparations requiring furnace work—for example, potassium cyanide, sodium sulphantimoniate, manganese, magnesium—the author could make his work more interesting. The more skillful students would thus be trained in manipulation which is quite within their power, but require more skill and practice than the preparations—with the exception of the anhydrous chlorides of aluminium and phosphorus—which are included in this book.

E. R.

TRAITE ELEMENTAIRE DE CHIMIE: (1) CHIMIE MINERALE, 366 pp.; (2) CHIMIE ORGANIQUE, 205 pp. PAR A. HALLER et P. TH. MULLER. Paris: Georges Carré, Éditeur. 1896.

These two volumes recall in size and arrangement Pinner's well-known "Repetitorien der Chemie," and doubtless will excellently serve the same purpose—that of preparing medical students, technical chemists, and pharmacists, for examination. The books are elementary, yet quite up to date. Such subjects as Raoult's methods of determining molecular weights, argon, carborundum, Moissan's furnace, carbides, pure hydroxylamine find mention in the first volume; the results of the late investigation of the sugars are included in the second. The presentation is very clear and compact; physical and stereo chemistry are not mentioned, but enough chemistry is given for those for whom the books are intended.

While the subject matter, printing, binding, and mechanical reproduction of the illustrations are thoroughly modern, the illustrations recall to the reviewer those happy days of youth, many years ago, when Stöckhardt's "Schule der Chemie" was a book in common use, and heating by gas was just introduced into laboratories. These illustrations recall those of Stöckhardt: the same picturesque charcoal-furnaces as source of heat; the same cork-stoppered U-tubes, serving as drying apparatus, and recalling the happy hours spent in making them air-tight; the same familiar open-top blast-furnace of fifty years ago. As historical and sentimental retrospect such pictures have value to a reviewer, but as a means of instruction to students their value is not great.

E. R.

THE PRINCIPLES AND PRACTICE OF AGRICULTURAL ANALYSIS. A manual for the examination of soils, fertilizers, and agricultural products. For the use of analysts, teachers, and students of agricultural chemistry. BY HARVEY W. WILEY, Chemist to the United States Department of Agriculture. Vol. II., FERTILIZERS. pp. vii, 322. Price, $2.00. Vol. III., AGRICULTURAL PRODUCTS. pp. xii, 666. Price, $3.75. Easton, Pa.: The Chemical Publishing Company.

The first volume of this work appeared about two years since and was noticed in this JOURNAL in December, 1895. The publication of the second and third volumes now rounds out a task for which the author has been well fitted, and which has been accomplished in a manner gratifying to chemists in general, and in particular to those dealing with agricultural materials and products. While treating primarily the analytical phase of the subject, the work will have a much broader application, and a distinct usefulness to the student of general chemistry.

The second volume is a presentation, as the author announces in the preface, of "a broad view of a great subject" and one which, so far as the writer has been informed, has not previously been attempted. The literature of fertilizer manufacture and analysis is scattered widely through technical and scientific journals, but has nowhere been so thoroughly compiled as in this volume. The fertilizer industry has from the first been subjected to rather rigid control by state laws regarding the certified composition of all such materials offered for sale. In this respect, public opinion has been expressed more forcibly than in the case of any other agricultural material. The analysis of commercial fertilizers has, therefore, assumed official and legal dignity in most of the states, resulting in the organization of an Association of Official Chemists, and the adoption of official methods for conducting such analyses. From a long-standing connection with this Association, the author has attained a commanding view of the entire subject which is well reflected in this volume.

The discussion of the subject is a rational one, treating under separate heads of the three fertilizing elements of commercial importance, *viz.*, phosphorus, nitrogen and potassium, as regards their commercial occurrence, origin, and chemical estimation. A separate section is devoted to the analysis of miscellaneous materials of fertilizing value. The work is comprehensive, citing with great detail not only the analytical methods officially adopted in this and other countries where fertilizer control is exercised, but also giving place to the presentation of obscure and unimportant methods of purely scientific interest. Much useful information not strictly analytical, is also incorporated, as for instance upon the history, manufacture and characteristics of basic phosphatic slags; upon the chemistry of the manufacture of phosphates; and upon the production of the famous Stassfurt potash salts.

The third volume, treating of Agricultural Products, embraces of course, a much wider field and the discussion of methods concerning which less uniformity of opinion prevails than in many other branches of analytical chemistry. The first part devotes about fifty pages to sampling, drying, incineration and extractions, which certainly cannot be thought too much for these important operations. The detection and estimation of carbohydrates and the examination of products containing them are discussed in not less than 300 pages. This includes an excellent description of polarimetric instruments and the scientific principles involved in their use and construction. All of the best known optical, volumetric, and gravimetric methods for estimating carbohydrates are presented exhaustively. Attention is also given to the examination of crude materials like cane and beets for factory purposes, as well as the various sugar-factory products.

The estimation of fats and oils is discussed in a separate section in which all of the physical tests for these bodies are fully described. Of special interest is the section devoted to the separation and examination of the various nitrogenous bodies of both vegetable and animal origin, in which the recent work of Osborne and his associates has been freely cited. The examination of dairy products, cereals, fodder, flesh, fruits, tea and coffee, tannin, tobacco, and fermented beverages are all amply discussed.

The estimation and calculation of the nutritive ratios and calorific values of food also receive due attention.

This enumeration may serve to show the comprehensive character of the work and, in a general way, its value. A closer examination will only strengthen the favorable opinion. The volumes are well bound and clearly printed on good paper. We are assured that the plates of the first edition have been destroyed, thus anticipating a revision for subsequent editions. There is little to criticise in the entire work and that only in regard to unimportant details. The whole is an exceedingly valuable contribution to chemical literature.

W. E. STONE.

VORLESUNGEN ÜBER BILDUNG UND SPALTUNG VON DOPPELSALZEN. BY J. H. VAN 'T HOFF. 8vo. 95 pp. Leipzig: Engelmann.

This publication is a systematic summary of the previously published investigations made in the author's laboratory, on the conditions of equilibrium in which double salts are involved. The book is divided into three parts. The first part consists of a concise graphical and algebraic discussion of the theoretical principles involved, constituting probably the most valuable feature of the work; the second part describes the various methods of determining the transition temperature; and the third part treats of applications of the general principles to a number of special double salts. There can be no question of the great value of monographs of this kind, of which this distinguished author is peculiarly prolific, to the investigator and advanced student of theoretical chemistry.

A. A. N.

AN OUTLINE OF THE THEORY OF SOLUTIONS AND ITS RESULTS. For Chemists and Electricians. By J. Livingston R. Morgan, Ph.D., (Leipzig) Instructor in Quantitative Analysis, Polytechnic Institute, Brooklyn. John Wiley and Sons, New York. Chapman and Hall, London. 1897. pp. 63.

This little book deals with some of the fundamental ideas underlying the present theory of solutions, in an elementary way. The four chapters are on: The Theory of Solution, The Methods for Determining Electrolytic Dissociation, The Theory of the Voltaic Cell, and Analytical Chemistry from the Standpoint of Electrolytic Dissociation. It is stated in the preface that "if by this sketch the author can induce anyone to go deeper into the subject, he will feel more than repaid for his work."

H. C. J.

UNIVERSITY of ILLINOIS.

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ON THE DECOMPOSITION OF DIAZO COMPOUNDS.

X.—A STUDY OF THE ACTION OF THE NITRATE AND SULPHATE OF PARADIAZOTOLUENE ON METHYL ALCOHOL UNDER VARIOUS CONDITIONS.[1]

BY WILLIAM E. CHAMBERLAIN.

The following pages contain an account of the action of paradiazotoluene nitrate and sulphate on methyl alcohol under various conditions of temperature and pressure, together with a study of the effect of sodium methylate, caustic potash, potassium carbonate, zinc dust, and zinc oxide on the course of the reaction.

Decomposition of Paradiazotoluene Nitrate with Methyl Alcohol at the Ordinary Atmospheric Pressure.

40 grams of paradiazotoluene nitrate were placed in a long-necked balloon flask of one liter capacity and covered with 100 cc. absolute methyl alcohol (from lime); the flask was then put into a water-bath and provided with a return-condenser. The decomposition began at the room temperature, but was very slow. On heating the water-bath to 55° C., the decomposition went on quietly and rapidly. When bubbles of nitrogen had ceased to appear, the alcohol was boiled for a short time to insure complete decomposition. In this way

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[1] From the Author's Thesis submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1894.

133 grams of diazo compound were decomposed with about 450 cc. absolute methyl alcohol.

The different portions were united and the alcohol boiled off. The alcoholic distillate was poured into five times its bulk of a saturated solution of sodium chloride. A yellow oil rose to the surface and was separated. The residue in the flask was made alkaline and distilled with steam, when a further quantity of yellow oil passed over. This was united with the oil from the alcoholic distillate, washed with caustic soda, then several times with water, dried with calcium chloride, and fractionated. A few drops came over between 100° and 130°, the main portion at 172°–177°, and about 2 cc. above 180°.

The lower-boiling fraction was tested for toluene by treatment with fuming nitric acid, and a liquid was obtained which had the odor of nitrobenzene. This was reduced in a test-tube with tin and hydrochloric acid, the whole made alkaline, and distilled with steam. An oil came over which had the odor of paratoluidine, but the quantity was too small for satisfactory testing.

The fraction boiling between 172° and 177° was redistilled several times, when it boiled at 174°.5 (cor.). 18 grams of a colorless, mobile oil were thus obtained. Its boiling-point corresponds to that of the methyl ether of paracresol (174°–175°) described by Körner.[1] To test further its identity, 2 grams of the oil were oxidized with potassium permanganate in alkaline solution, and an acid obtained which melted at 184° (cor.). This agreed fairly well with the melting-point given for anisic acid (185°). The oil is therefore the methyl ether of paracresol, $CH_3.C_6H_4.OCH_3(p)$.

The fraction of the oil which came over above 180° was found to have no definite boiling-point, and was probably a complex mixture. Nothing was done with it.

The residue in the steam-flask was acidified with sulphuric acid and again distilled with steam. Nothing came over except water.

The contents of the steam-flask were poured out and the liquid evaporated. Nothing was found but sodium sulphate.

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[1] Ztschr. Chem., 1868, 326.

The tar—a black, solid mass—was extracted with petroleum ether (boiling-boint 80°) after several other solvents had been tried, and 3 grams of a yellow solid obtained, which, on recrystallizing several times from petroleum ether and from alcohol, melted at 80°.5 (cor.). The crystals obtained from petroleum ether were long, flat needles with serrated edges. These were not brittle, and were consequently difficult to powder. The crystals obtained from alcohol were fine, sharp needles which were quite brittle.

The melting-point and other physical properties of this substance made it probable that it was identical with the dinitroparacresol (melting-point 85°) obtained by Städel by action of nitric acid upon the ethyl ether of paracresol.[1] To prove its identity the potassium salt was made, from it the silver salt, and from this, by treatment with ethyl iodide in a pressure-bottle, the ethyl ether. This substance agreed with the description given by Städel of the ethyl ether of paracresol. The melting-point found was 71°; that given by Städel is 75°.

The relative difference between the melting-points of the dinitrocresol and of its ethyl ether, as found by Städel and myself, is the same. I judge, therefore, that the difference is due to the thermometers. The thermometer used throughout this investigation was carefully compared with a standard thermometer for temperatures between 14° and 92°. Temperatures near 183° were corrected by the boiling-point of aniline.

The melting-point of dinitroparacresol (CH_3, NO_2, OH, $NO_2 = 1, 3, 4, 5$) is given by different investigators variously as 79°, 80°,[2] 82°,[3] 83°,[4] 83°.5,[5] 84°,[6] 85°.[7] To test the melting-point with more accuracy, a quantity of dinitrocresol was prepared. 36 grams of paracresol were diluted with 36 grams glacial acetic acid. 54 grams nitric acid (sp. gr. 1.4) were diluted with 108 grams glacial acetic acid. The two solutions were dropped slowly from dropping-funnels into a flask surrounded by a freezing-mixture. After several hours the

[1] Ann. Chem. (Liebig), **217**, 163.

[2] Ber. d. chem. Ges , **13**, 1946.

[3] *Ibid*, **6**, 974.

[4] *Ibid*, **7**, 1023; **14**, 568.

[5] *Ibid*, **7**, 536.

[6] *Ibid*, **2**, 207: **8**, 685; **14**, 986; Ann. Chem. (Liebig), **173**, 205.

[7] Jsb., 1866, p. 360.

mixture was warmed on a water-bath and poured into much cold water. A yellow solid separated out. It was distilled with steam to free it from the more volatile mononitrocresol. The residue in the steam-flask, consisting wholly of dinitroparacresol, was recrystallized from alcohol until repeated recrystallization failed to make any change in the melting-point. The melting-point of the dinitroparacresol was found to be constant at 80°.5 (cor.).

Action of Nitric Acid on Paramethoxytoluene.

In view of the fact already mentioned, that Städel obtained dinitroparacresol from paraethoxytoluene by action of nitric acid, it was thought that the action of nitric acid, both dilute and concentrated, upon paramethoxytoluene would also prove of interest. 10 grams of paramethoxytoluene and 20 grams pure nitric acid (sp. gr. 1.4) were each diluted with 20 grams glacial acetic acid. The two solutions were dropped slowly into a flask surrounded with ice and allowed to stand over night. In the morning the solution was poured into much cold water and the whole allowed to stand. The next day the water had cleared up, and at the bottom was an oil which was full of crystals. These were separated from the oil by the filter-pump, and recrystallized from alcohol. They melted at 80°.5. This showed them to be dinitroparacresol. To establish the identity of this substance, the ethyl ether was made as before. It melted at 71°.

The quantity of oil from which the crystals were separated was so small that nothing more was done with it. Some work done later makes it probable that it was mononitrocresol.

10 grams of paramethoxytoluene were poured slowly from a dropping-funnel on to 40 grams pure concentrated nitric acid, in a flask provided with a return-condenser. Heat was applied to start the reaction. Abundant red fumes were given off. After some time the reaction became somewhat less violent, and 20 grams of fuming nitric acid were added and the rest of the ether was run in. 10 grams of concentrated nitric acid and 20 grams of concentrated sulphuric acid were then added and the mixture boiled until the red fumes

ceased to appear. The whole was then poured into cold water, and after a time the oil which first separated out became partially solid. The crystals were separated from the oil by the filter-pump, and recrystallized from alcohol. They melted at 122°. The crystals were needles of a slightly yellowish color. They looked like the ethyl ether of dinitroparacresol. The melting-point showed them to be the methyl ether of dinitroparacresol. The yield was very small, only 0.2 gram of purified substance. Most of the ether had been oxidized completely by the strong nitric acid.

The action of dilute nitric acid upon paramethoxytoluene is, thus, not only to introduce the nitro groups, but also to saponify the ether. This is what one would expect from the work of Städel. From paracresol ethyl ether he obtained dinitroparacresol and dinitroparacresol ethyl ether[1]; from orthocresol ethyl ether he obtained almost exclusively dinitroorthocresol[2]; from paracresol benzoyl ether, dinitroparacresol.[3] This reaction of dilute nitric acid is somewhat surprising. Saponification does not usually result from such mild treatment. Some of the dinitrocresol ethyl ether was boiled with moderately dilute nitric acid for several hours without any effect whatever. It is probable that, when the nitro groups are entering, the equilibrium of the molecule is so disturbed that saponification is effected by means which do not ordinarily produce that result.

Another experiment was made with 205 grams of paradiazotoluene nitrate, in the hope of determining more accurately the character of the reaction with methyl alcohol, both as to the yield of ether and also as to the other substances formed. The decomposition and study of the products were carried on as before described. The oil separated into three fractions: one, about 1 cc., boiling at 100°–130°; the main portion, about 40 grams, boiling at 173°–177°, most of it at 175°; and about 2 cc., boiling at 215°–225°. There was some tar left in the bulb at 260°.

The fraction boiling at 100°–130°, supposed to be toluene, was boiled with strong nitric and sulphuric acids until action ceased, and then the whole was poured on ice. A white solid separated out, which was recrystallized from alcohol and found to melt at 70°.5. This is ordinary dinitrotoluene (2, 4), and proves the presence of toluene among the decomposition-products of the diazo compound.

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[1] Ann. Chem. (Liebig), **217**, 161.

[2] *Ibid*, **217**, 168.

[3] *Ibid*, **217**, 180.

The fraction boiling at 215°–225° (only about 2 cc.) was oxidized with potassium permanganate, in the hope that a crystalline substance might be obtained which would identify it. A few white crystals looking something like urea were obtained, which melted at 181° (cor.), but the quantity was too small to permit of an analysis.

The tarry residue in the steam-flask was extracted with petroleum ether, as before, and 5.5 grams of dinitroparacresol obtained, melting at 80°.5. The residues and distillates were thoroughly worked over, but nothing further was found in them.

The main product of the reaction between methyl alcohol and paradiazotoluene nitrate at the ordinary atmospheric pressure is paramethoxytoluene. A very small quantity of toluene is also formed, due, probably, to the action of the nitric acid liberated in the reaction. The reaction thus consists mainly in the substitution of the methoxyl for the diazo group :

$$CH_3.C_6H_4.N_2.NO_3 + CH_3OH = CH_3.C_6H_4.OCH_3 + HNO_3 + N_2.$$

The presence of toluene is accounted for by the reaction :

$$CH_3.C_6H_4.N_2.NO_3 + CH_3OH = C_6H_5.CH_3 + CH_2O + HNO_3 + N_2.$$

There was no odor of formaldehyde perceived during the decomposition, and no indication of the presence of formaldehyde or if its polymers was found among the products of decomposition.

Decomposition of Paradiazotoluene Sulphate with Methyl Alcohol at the Ordinary Atmospheric Pressure.

47 grams of paradiazotoluene sulphate were placed in a flask provided with a return-condenser, together with 200 cc.

absolute methyl alcohol, and the flask placed in a water-bath. The decomposition did not begin until the boiling-point of the alcohol was reached. The evolution of nitrogen went on quietly and steadily, and in about half an hour the decomposition was complete.

60 grams of diazotoluene sulphate were decomposed, in the same way, with 250 cc. absolute methyl alcohol.

The two portions were united and the alcohol boiled off. The distillate was treated with salt solution and a yellow oil separated. The distillation was then continued with steam, and the yellow oil which came over separated and united with that from the alcoholic distillate. The yield of crude oil was 40 grams. On fractionating, almost all of the oil came over at 170°–180°, and, on redistilling, at 174°–176° (cor.). This is, again, the methyl ether of paracresol.

A few drops of oil distilled over below 170°, and when redistilled, 5 or 6 drops came over at 100°–130°. These were treated with strong nitric and sulphuric acids, and crystals obtained melting at 70°, proving the presence of a minute quantity of toluene among the decomposition-products.

A small quantity of yellow oil distilled above 180°. An unsuccessful attempt was made to get crystals from it. The quantity of tar left in the steam-flask was very small, compared with that obtained in the decomposition of the diazo nitrate.

Part of the liquid in the steam-flask was neutralized with barium carbonate and filtered. Addition of sulphuric acid to the filtrate produced a slight cloudiness, probably due to the presence of a sulphonic acid, as any methylsulphuric acid, if formed, would have been decomposed by the steam.

The reaction with the diazo sulphate is, again, the methoxy reaction, almost exclusively. The reaction is much cleaner than is the case with the nitrate, and the yield of methoxytoluene is much larger.

Decomposition of Paradiazotoluene Nitrate with Methyl Alcohol under Diminished Pressure.

In this experiment, 41 grams of paradiazotoluene nitrate were decomposed with 120 cc. of absolute methyl alcohol.

The flask was connected with a return-condenser, the upper end of which was joined to a suction-pump and a manometer. During the experiment the manometer showed a depression of 490–500 mm. Slight signs of decomposition were observed at the ordinary temperature. At 40° the decomposition went on steadily. The escaping gases were passed through water, and the water was tested for an aldehyde with ammoniacal silver nitrate, but no indication of an aldehyde was found.

The products were studied as above described, first boiling off the alcohol, then making the contents of the flask alkaline, and distilling with steam. The yellow oil which came over separated, when distilled, into two fractions, one boiling at 105°–112°, and the other at 172°–177°, showing that here, again, toluene and methoxytoluene were the products of decomposition. The yield was better than in the experiment with the nitrate at ordinary pressure—6 cc. of ether and 2 of toluene. There was a small quantity of oil left in the distilling bulb at 180°. This was found to contain toluidine which had not been diazotized.

When the distillate from the steam-flask came over clear, the contents of the flask were acidified and steam again passed through. About 2 cc. of a dark-red oil distilled over, which solidified when placed in a freezing-mixture. The mass was put on a drying-plate and the crystals dissolved in alcohol. On cooling the alcohol they reappeared, and were separated and dried (melting-point 32°). The substance looked and smelled like orthonitrophenol. Treated with caustic soda its solution turned red. It was very soluble in alcohol and was volatile with boiling alcohol. These properties show that it is the mononitro derivative of paracresol (CH_3, NO_2, $OH = 1, 3, 4$).

The differences noted between this reaction and the one at ordinary pressure were such as were to be expected. The reaction was cleaner than the one at ordinary pressure, probably due to the lower temperature, and the nitro compound formed did not contain two nitro groups. It is to be noted, also, that the proportion of toluene was greater than in the reaction at ordinary pressure.

Decomposition of Paradiazotoluene Sulphate with Methyl Alcohol under Diminished Pressure.

Using the same method as in the preceding experiment, 57 grams of paradiazotoluene sulphate were decomposed with 250 cc. of absolute methyl alcohol, with a diminution from the ordinary pressure of 500 mm. The decomposition took place slowly when the methyl alcohol was heated up to its boiling-point, and was complete in about four hours. The alcohol was distilled off, the residue distilled with steam, and the oil from the different portions united. The yield of crude oil was 25 grams. On fractioning, a few drops came over between 100° and 120°, showing a slight trace of toluene. Almost the whole of the oil passed over between 172° and 177°. Only a very small quantity of tar was formed.

The reaction in this case is a very clean one. Methoxytoluene is the main product, with only a slight trace of toluene.

Decomposition of Paradiazotoluene Nitrate with Methyl Alcohol under Increased Pressure.

The experiments in which increased pressure was used were carried on in a balloon flask surrounded with wire netting. The flask was fitted with a 2-hole rubber stopper, and connection was made with a safety-valve and a manometer. By changing the weight on the safety-valve the pressure could be kept at any desired point.

In this way 46 grams of paradiazotoluene nitrate were decomposed with 200 cc. of absolute methyl alcohol, with an increase over the ordinary atmospheric pressure of 500 mm. Heat was applied, and the decomposition went on slowly and steadily at about 35°.

After the decomposition was finished the alcohol was distilled off under reduced pressure. On adding salt solution to the distillate only a very small quantity of oil separated. The contents of the flask were then made alkaline and distilled with steam. At first the distillate consisted only of water and oil. Soon, however, a very small quantity of orange-colored solid appeared in the condenser. The distillation with steam was continued till the distillate became clear, when the contents of the steam-flask were made acid with sulphuric acid, and the distillation with steam continued. A reddish oil now distilled over, which solidified in the receiver. The residue of tar was smaller than was the case when the decomposition took place at the ordinary pressure.

On fractionating the oil, no trace of toluene was found. Most of the oil—12 grams—passed over between 172° and 177°. A small quantity was left in the distilling bulb above 180°. This was poured into a small beaker and cooled in a freezing-mixture, when crystals appeared in it. These were filtered off and recrystallized from alcohol. They melted at 112°, and had the other properties of mononitrotoluidine. Their formation here was due to the action of the nitric acid upon a little undiazotized toluidine. About half a gram of this substance was obtained. This is the same as the red solid which distilled over from the alkaline solution.

The solid which distilled over from the acid solution was recrystallized from alcohol and found to melt at 32°. It was identical with the mononitrocresol obtained when working at reduced pressure. The yield was only 1.1 grams. Nothing crystallizable could be extracted from the tar.

The occurrence of mononitrocresol instead of dinitrocresol in this experiment is due, probably, to the fact that the alcohol was boiled off under reduced pressure, and the action of the nitric acid on the cresol ether was therefore not so energetic as when the alcohol was boiled off at a higher temperature.

Decomposition of Paradiazotoluene Sulphate with Methyl Alcohol under Increased Pressure.

In this experiment 66 grams of paradiazotoluene sulphate were decomposed with 200 cc. of absolute methyl alcohol under an increase of 550 mm. over the ordinary atmospheric pressure. The decomposition began at about 60°. The alcohol was boiled off and steam passed through the residue, exactly as in the case of the nitrate, except that the contents of the flask were not made alkaline. Yield of crude oil, 25 grams. On fractionating, a few drops came over below 140°, and were proved to contain toluene by making the dinitro derivative and testing the melting-point. Almost all of the oil distilled at 172°–177°. About 1 cc. of dark-red oil remained above 180°. This would not crystallize, and nothing was done with it. There was less tar formed in this reaction than in any other so far performed.

Here, again, the reaction consists almost entirely in the introduction of the methoxyl group.

Decomposition of Paradiazotoluene Nitrate with Sodium Methylate.

The work of Beeson[1] on the action of the diazobenzene nitrate and sulphate with sodium methylate, and with methyl alcohol in the presence of caustic potash and of zinc dust, made it probable that paradiazotoluene nitrate and sulphate would give the hydrogen reaction in the presence of these and similar substances.

44 grams of paradiazotoluene nitrate were added gradually to 200 cc. methyl alcohol in which 15 grams of sodium had been dissolved. The decomposition took place at once, with separation of sodium nitrate. The flask was kept in ice-water during the decomposition. The products of the decomposition were distilled with steam. 9 grams of crude oil were obtained. This proved to be toluene. Only a few drops of dark-red liquid remained in the distilling-bulb above 120°. This was probably tar carried over mechanically by the steam and dissolved by the toluene. There was a considerable quantity of dark-brown tar left in the steam flask. This showed minute crystals scattered through it, but all attempts to separate the crystals were unsuccessful.

In this case, as in the similar one studied by Beeson, the hydrogen reaction is the only one which takes place.

Decomposition of Paradiazotoluene Sulphate with Sodium Methylate.

52 grams of paradiazotoluene sulphate were decomposed with 200 cc. methyl alcohol in which 12 grams of sodium had been dissolved. The method of procedure was the same as in the case of the nitrate. The yield of oil was small—7.5

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[1] This JOURNAL, **16**, 244.

grams. On distilling, practically all of it came over at 109°–111°. The main product of the reaction was tar, from which nothing could be obtained. This was to be expected, for Beeson could get nothing but tar from the reaction between sodium methylate and diazobenzene sulphate.

The reaction in this case, as with the nitrate, is the hydrogen reaction exclusively.

Decomposition of Paradiazotoluene Nitrate with Methyl Alcohol and Caustic Potash.

45 grams of paradiazotoluene nitrate were decomposed with 200 cc. methyl alcohol, in which 20 grams of pure caustic potash had been dissolved. The diazo compound was added very slowly and in small portions, the flask being shaken after each addition. The decomposition took place immediately, but at first the action was very slow. Soon, however, enough heat was furnished by the reaction to make it necessary to moderate the action by cooling the flask. The whole was let stand over night, and the next day boiled for a short time on the water-bath, to insure complete decomposition. The alcohol was boiled off and the residue distilled with steam. By far the greater part of the oil came over with the alcohol. Yield of crude oil, 11 grams. Practically, the whole of this came over between 107° and 114°, and all but a few drops at 109°. A few drops of tarry oil remained in the bulb. The amount of tar left in the steam-flask was considerable.

The reaction is here, as was expected, entirely the hydrogen reaction.

Decomposition of Paradiazotoluene Sulphate with Methyl Alcohol and Caustic Potash.

In the same way 48 grams of paradiazotoluene sulphate were decomposed with 200 cc. methyl alcohol and 25 grams pure caustic potash. Yield of crude oil, 13 grams. This distilled over at 105°–115°. Nothing was done with the tar. Here, as before, the hydrogen reaction alone takes place.

Another experiment was performed, in which heat was applied. The decomposition took place very rapidly, and the products of the reaction were, besides tar, toluene and methoxytoluene in about equal quantities. This would tend to confirm the idea that heat is favorable to the alkoxy reaction.

Decomposition of Paradiazotoluene Nitrate with Methyl Alcohol and Potassium Carbonate.

In exactly the same way as above, 37 grams of paradiazotoluene nitrate were decomposed with 150 cc. methyl alcohol and 40 grams anhydrous potassium carbonate. The decomposition took place without the aid of heat. The alcohol was boiled off and steam passed through the residue. When the distillation with steam was nearly ended, a very little reddish oil containing crystals appeared in the condenser. The quantity was so small that nothing could be done with it. 11 grams of crude oil were obtained, which distilled over between 107° and 114°.

The effect of an alkaline carbonate upon the course of the reaction is, thus, the same as that of a caustic alkali.

Decomposition of Paradiazotoluene Sulphate with Methyl Alcohol and Potassium Carbonate.

40 grams of paradiazotoluene sulphate were decomposed with 300 cc. methyl alcohol and 40 grams anhydrous potassium carbonate. The method was the same as above given. Yield of crude oil, 10 grams. This proved to be toluene.

Decomposition of Paradiazotoluene Sulphate with Methyl Alcohol and Zinc Dust.

Beeson[1] obtained benzene and diphenyl as products of the decomposition of diazobenzene nitrate with methyl alcohol and zinc dust. The following experiments were made, to see whether the corresponding products would be formed in the case of diazotoluene sulphate and nitrate.

46 grams of paradiazotoluene sulphate were added gradually to 130 cc. methyl alcohol and an excess of zinc dust. Decomposition took place at once, and was moderated by putting the flask into ice-water. The products were treated with steam in the usual manner. Yield of crude oil, 9.5 grams. This proved to be toluene. No tar was observable in the steam-flask after the oil had all distilled over. The residue

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[1] This JOURNAL, **16**, 252.

was extracted with ether, in the hope that ditolyl might be obtained. On boiling off the ether about 5 grams of a clear, yellow, gummy substance were obtained, which was probably a complex mixture. All efforts to separate something which could be identified were unsuccessful.

Decomposition of Paradiazotoluene Nitrate with Methyl Alcohol and Zinc Dust.

Exactly as in the preceding experiment, 38 grams of paradiazotoluene nitrate were decomposed with 130 cc. methyl alcohol and an excess of zinc dust. The oily product proved to be toluene, and the yield was about the same as in the preceding experiment. The residue was extracted with ether, as before ; nothing but tar was found.

During the course of this experiment it was noticed that when fresh zinc dust was added to the mixture of zinc dust, methyl alcohol and diazo compound, there was immediately a more rapid evolution of nitrogen, although an excess of zinc dust was already present. It was thought that perhaps this might be due to the more energetic action of the zinc oxide which is always present in small quantity in zinc dust. To test the influence of the oxide upon the course of the reaction, experiments were made with the diazo nitrate and sulphate with methyl alcohol in the presence of zinc oxide.

Decomposition of Paradiazotoluene Sulphate with Methyl Alcohol and Zinc Oxide.

44 grams of paradiazotoluene nitrate were added gradually to 200 cc. methyl alcohol and 20 grams powdered zinc oxide. No decomposition took place at the room temperature. The flask was placed in a water-bath, provided with a return-condenser, and heated slowly. Decomposition began at about 40°, and went on quietly and slowly, as when alcohol alone was used. After some time, however, the action had to be kept back by taking the flask out of the bath. The volatile products were separated in the usual way. The yield of crude oil was 10 grams. On fractionating, this was found to consist of about equal parts of toluene and methoxytoluene. The residue in the steam-flask was unpromising, and nothing was done with it.

Decomposition of Paradiazotoluene Sulphate with Methyl Alcohol and Zinc Oxide.

54 grams of paradiazotoluene sulphate were decomposed, as in the preceding experiment, with 250 cc. methyl alcohol and 20 grams powdered zinc oxide. The decomposition phenomena were similar to those in the case of the nitrate. After the decomposition had well begun, the mixture thickened and became quite pasty, and the bubbles of escaping nitrogen caused it to swell up so as nearly to fill the flask. After a time the mass became more liquid again. The products of decomposition were distilled with steam. Yield of crude oil, 17 grams. This consisted of about two parts of toluene and one of methoxytoluene.

Zinc oxide evidently does not influence the course of the reaction so strongly as does zinc dust. Just what is the full course of the reaction with zinc dust and with zinc oxide is not known. Want of time has prevented a more exhaustive study of these two reactions.

Comparison of Reactions.

The quantities obtained in the above described reactions are significant only in a general way, still it is of interest to compare them as far as the data will allow. The percentages of the theoretical yield are given.

	Paramethoxy-toluene.	Toluene.
Nitrate with alcohol, ord. pressure	29	trace
Sulphate “ “ “	66	trace
Nitrate “ dim. “	22	10
Sulphate “ “ “	77	trace
Nitrate “ incr. “	39	....
Sulphate “ “ “	61	trace
Nitrate with $NaOCH_3$	..	36
Sulphate “	..	32
Nitrate with alcohol and KOH	..	44
Sulphate “ “	..	59
Nitrate “ K_2CO_3	..	53
Sulphate “ “	..	44
Nitrate “ zinc dust	..	*
Sulphate “ “	..	46
Nitrate “ zinc oxide	17	22
Sulphate “ “	20	48

* No record; about the same as the sulphate.

There may, of course, have been traces of methoxytoluene in those cases in which toluene was the only product found; but, as no method suggested itself for detecting traces of methoxytoluene in mixtures, no proof of its presence was found.

Summary of Results.

Several conclusions seem to be justified by the results of the experiments described in this paper.

1. The suggestion of Remsen and Dashiell,[1] that lowering of temperature and pressure tends to favor the hydrogen reaction, find support in the reaction of the diazo nitrate under diminished pressure. The sulphate, too, gives a better yield of methoxy product than the nitrate, and it decomposes at a higher temperature. But the sulphate gives a better yield of methoxy product as the pressure decreases. The largest percentage of methoxy product is given by the sulphate under reduced pressure.

2. The action of dilute nitric acid upon paramethoxytoluene, forming dinitrocresol, makes it probable that, in the cases in which nitrophenols are formed by the reaction of diazo nitrates with alcohol, these products are formed by saponification of the ethers first formed, the introduction of nitro groups taking place at the same time.

3. The fact that these diazo salts do not decompose rapidly at a low temperature in the presence of caustic potash was unexpected and surprising. It may find its explanation in the formation of isodiazo compounds similar to those first studied by Schraube and Schmidt.[2]

4. The results obtained by Beeson,[3] by the use of alkalies and of zinc dust, were found to hold good in all the cases studied, with the exception that no ditolyl was found. Any substance which will neutralize the acid liberated in the decomposition of the diazo compound will probably determine the hydrogen reaction, at least to some extent. This may be due to the fact that the reaction takes place at a lower temperature. When zinc oxide was used, the temperature at

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[1] This JOURNAL, **15**, 124.

[2] Ber. d. chem. Ges., **26**, 514.

[3] This JOURNAL, **16**, 252.

which decomposition took place was higher than in the other cases in which neutralizing agents were used, and the product was a mixed one, the reaction taking place in both ways. Why zinc should be more effective than zinc oxide, it is hard to say. Equations can be written which account for all the substances found, but they are of little value in the present state of knowledge.

XI.—THE REACTION OF SALTS OF THE NITRODIAZOBENZENES AND THE DIAZOBENZOIC ACIDS WITH METHYL ALCOHOL.[1]

BY GEORGE F. WEIDA.

The special object of this work was the study of the decomposition with methyl alcohol of the diazo compounds obtained from the three nitranilines and the three aminobenzoic acids, and the comparison of the results obtained with those obtained by Remsen and Graham[2] with the same diazo compounds and ordinary alcohol.

A. THE NITRODIAZOBENZENE SALTS.

1. *Orthonitrodiazobenzene Sulphate.*

Preparation of Orthonitraniline.—After trying various methods for the preparation of this substance, I should recommend the following as most advantageous:

The nitration is effected by the method of Körner—as described[3] by Remsen and Graham—except that a stronger nitric acid may be used. I found that by cooling properly, an acid of specific gravity 1.475–1.478 could be used without losing any considerable quantity of material by too rapid nitration. The contents of the beaker are now thrown into an evaporating-dish containing lumps of ice. The solid product is filtered from the ice-water as soon as practicable and treated as described by Remsen and Graham. But inasmuch as the filtrate contains the greater portion of the orthonitracetanilide,[4] it is very important to extract it and add it to the solid which has been filtered off from the ice-water. This is best effected by extraction of the filtrate with chloroform and subsequent evaporation of the chloroform extract. In the distillation with steam, utilize the saturated aqueous solution of orthonitraniline from the distillate to supply the boiler, according to the suggestion of Lellman. Avoid too great an excess of alkali to break off the acetyl group from the nitracetanilide, as prolonged boiling with excess of alkali is apt to yield nitrophenol.[3]

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[1] From the Author's Thesis, submitted to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy, June, 1894.

[2] This JOURNAL, **11**, 319.

[3] *Loc. cit.*

[4] Grethen: Ber. d. chem. Ges., **9**, 775.

Preparation of Diazo Compouud from Orthonitraniline.—The nitraniline was suspended in dilute nitric or sulphuric acid, and, the vessel being placed in a freezing-mixture, a rapid current of nitrous fumes was passed through the mixture until it was saturated. I then added well cooled alcohol and ether to the solution, and after some time the diazo compound crystallized out. Inasmuch as sulphuric acid yielded the better results, I used the diazo compound obtained by mixing 45 cc. of the dilute and 5–8 cc. of strong sulphuric acid for every 10 gram portion af the orthonitraniline taken. 10 grams of nitraniline gave 14–15 grams of diazo compound.

Decomposition with Methyl Alcohol.—64 grams of the diazo compound, prepared as just described, were decomposed with 500 cc. methyl alcohol in three separate portions. The flask containing the alcohol and diazo compound was in each case connected with an inverted condenser, and then heated on the water-bath. Decomposition began as soon as the temperature of the water-bath reached 35°–40°—much lower than with the nitrates of the corresponding meta and para diazo compounds. At 60° the reaction went on very rapidly, and it was necessary to regulate the heat carefully. When the reaction became less vigorous the water in the bath was heated to 100°, and kept there for some time.

The products of decomposition from these flasks were united and the methyl alcohol distilled off on the water-bath. The liquid remaining in the flask was treated with an excess of an aqueous solution of caustic soda and subjected to distillation with steam. The distillate contained about 23 cc. of an oil, which (after drying with calcium chloride) had the boiling-point of nitrobenzene. 23 cc. of pure nitrobenzene (27.6

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[3] Ber. d. chem. Ges., 7, 76.

grams) corresponds to 87 per cent. of the theoretical yield from 64 grams of orthonitrodiazobenzene sulphate. No other definite chemical compounds were obtained either from the distillate or from the residue in the flask.

It is worthy of note that with this large yield of nitrobenzene the boiling-point of the product was much more constant than that of the oil obtained from the meta- and paranitrodiazobenzene nitrates.

2. *Metanitrodiazobenzene Nitrate.*

Decomposition with Methyl Alcohol.—After several preliminary tests with smaller quantities of diazo compounds, 120 grams of the substance were decomposed (in portions) by heating on the water-bath in a flask connected with an inverted condenser. The temperature was gradually raised to the boiling-point of water, and the heating was always continued for at least an hour—some considerable time after the evolution of gas had ceased. On cooling there was found in almost every case a beautiful yellowish-brown crystalline powder in a reddish liquid. The solid product was filtered off and its properties were studied. To my surprise it was found to be explosive and to behave in many respects as a diazo compound would do under similar conditions. Yet it seemed incredible that a portion of the diazo compound should remain unchanged after prolonged boiling with a large excess of methyl alcohol, and that it should crystallize out from the clear solution. When it was found, however, that it decomposed further with fresh portions of methyl alcohol (not only over the free flame, but even on the water-bath) it was concluded that such must be the case. The solid was accordingly decomposed with fresh portions of methyl alcohol, and the products of decomposition were added to the liquid before mentioned.

The united liquids representing the decomposition-products of 120 grams of metanitrodiazobenzene nitrate were treated as follows: The methyl alcohol was distilled off on the water-bath. 30 grams of caustic soda dissolved in 200 cc. of water were added to the residue to make it alkaline. On distillation with steam an abundance of an oily liquid passed over with the water, accompanied by a small quantity of a whitish powder. The latter portion of the distillate was caught separately, and from it after a time a few long needles crystallized out. These needles had the melting-point 37°, agreeing with that given for metanitranisol.[1] The other portions of light solid were recrystallized from alcohol and also had the melting-point 37°. This indicates the formation of small quantities of metanitroanisol.

The oil which came over with the first portions of the distillate was separated from water by means of a separating-funnel. It measured about 30 cc. After drying with calcium chloride, the greater portion distilled from 208°–210°, but some continued to come over at higher temperatures, almost up to 254°, the boiling-point of the nitranisol. If we assume that there were 36 grams of pure nitrobenzene, this would correspond to 51 per cent. of the theoretical yield if all the diazo compound could pass over into nitrobenzene.

After distillation with steam, the contents of the flask were acidified with dilute sulphuric acid, and were again subjected to distillation with steam. It was impossible, however, to isolate any further definite compounds either from this distillate or from the tarry residue remaining behind in the flask.

3. *Paranitrodiazobenzene Nitrate.*

First Decomposition with Methyl Alcohol.—Portions of about 20 grams of the diazo compound, prepared as just described, were decomposed with methyl alcohol, from 7–10 cc. of the alcohol being used for each gram of diazo compound. The flasks in which these portions were placed were connected with inverted condensers and heated on the water-bath. Decomposition began when the temperature of the water-bath reached about 60°. After the reaction became less marked, the temperature of the water-bath was gradually raised to 100°, and kept there for some time. The contents of each flask after the end of the decomposition consisted of a clear solution of the products of decomposition.

Three of these portions, corresponding to 57 grams of the diazo compound, were united and the methyl alcohol distilled off on the water-bath. The residue was made alkaline with about 13 grams of caustic soda dissolved in 300 cc. of water. This alkaline mixture was then subjected to distillation with steam. The receiver was well cooled with snow and ice, in order that any paranitranisol that came over might be obtained as a solid. The first portions of the distillate contained about 13 cc. of an oily liquid, which was shown by its boiling-point to be mostly nitrobenzene, but containing a small portion of a substance of high boiling-point, probably paranitranisol. Assuming a yield of 13 cc. (15.6 grams) of pure nitrobenzene, this would correspond to about 47 per cent. of the theoretical yield if all the diazo compound could pass over into nitrobenzene. The latter portions of the distillate contained a white solid in much greater quantity than was the case with the corresponding meta compound. It was collected and dried on filter-paper and found to weigh 3.2 grams. On purification it was found to correspond in melting-point,[1] etc., to the properties ascribed to paranitranisol. 3.2 grams of paranitranisol correspond to about 8 per cent. of the theoretical yield.

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[1] Bantlin: Ber. d. chem. Ges., 11, 2101.

Second Decomposition with Methyl Alcohol.—70 grams of the diazo compound were decomposed and the products of decomposition were treated as described above, except that more caustic soda was required to make the mixture alkaline. The products were the same as before, but in somewhat different proportions. About 13.5 cc. of the oil were obtained and 8.7 grams of the white solid product. As before, most of the oil boiled at the boiling-point of nitrobenzene, but the thermometer gradually rose, showing the presence of some small quantity of paranitranisol mixed with the nitrobenzene. In fact, I obtained some nitranisol from these portions of higher boiling-point and recrystallized it. This, as well as the main portion of the solid first obtained after recrystallization, was found to have the melting-point of paranitranisol[2] (53°). If the above named quantities are considered as representing pure nitrobenzene and nitranisol respectively, they correspond to about 40 per cent. of the theoretical yield for nitrobenzene, and 17 per cent. of the theoretical yield for the nitranisol.

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[1] J. prakt. Chem., **141**, 153.

[2] Willgerodt: J. prakt. Chem., **141**, 153.

B. THE SALTS OF THE DIAZOBENZOIC ACIDS.

1. *Orthodiazobenzoic-acid Nitrate.*

Preparation of the Diazo Compound from Anthranilic Acid.—The diazo compound was prepared according to the method of Griess[1] as follows: A pasty mixture of 10 grams of anthranilic acid (orthoaminobenzoic acid) with 50–60 cc. of nitric acid which had been previously diluted with an equal volume of water, was cooled in a freezing-mixture, and nitrous fumes were passed through it until everything had gone into solution, and there was an excess of nitrous acid present. About 150 cc. each of alcohol and ether were then added. The diazo compound separated out after stirring for some minutes. It was collected, washed with ether and dried in the usual manner. 10 grams of acid yielded from 10–11 grams of diazo compound. The product was yellowish, readily soluble in water, and when heated on platinum foil it exploded with a faint report.

Decomposition with Methyl Alcohol.—42 grams of diazo compound, prepared as just described, were placed in a flask and covered with about 200 cc. of methyl alcohol. The flask was connected with an inverted condenser, and heated on the water-bath. Decomposition began when the temperature of the bath reached 60° and went forward rapidly. After the methyl alcohol was distilled off, 100 cc. of water were added, and an oil sank beneath the water. Suspecting the formation of ethereal salts and wishing to separate them from any acid that might be volatile with steam, it was necessary to neutralize the free acid before distillation. In order to effect the neutralization without saponifying the ethereal salts, precipitated carbonate of calcium was used instead of the usual caustic alkali.

After carefully neutralizing all the free acid, the contents of the flask were subjected to distillation with steam. A yellow oil was separated from the aqueous portion of this distillate.

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[1] Ber. d. chem. Ges., 9, 1653.

and was found to measure about 10 cc. If this oil is an ethereal salt it is most probably either methyl benzoate, which boils at 199°, or the methyl ether of methylsalicylic acid (methyl orthomethoxybenzoate) which boils at 244°–246°. The oil was dried with calcium chloride and distilled. The thermometer rose gradually until it reached a maximum at 245°, and at this temperature the remainder of the oil distilled over. This shows that the oil is not a pure chemical individual, although it probably contains methyl orthomethoxybenzoate. The oil is not readily saponified by boiling with caustic alkali in a test-tube, but saponification is effected by boiling for some time in a flask connected with an inverted condenser. By diluting the strongly alkaline liquid thus obtained with water, and neutralizing with hydrochloric acid, a white acid was precipitated. Recrystallized from boiling water, it was obtained in beautiful crystals melting at about 88°. By repeated recrystallization the melting-point was raised to 99°. This therefore seems to be orthomethoxybenzoic acid, and confirms the probability that the oil from which it is obtained is mostly methyl orthomethoxybenzoate. The quantity of acid remaining after the repeated recrystallization was so small that it could not be investigated satisfactorily.

After the distillation with steam, the liquid remaining behind in the flask was also examined. Hydrochloric acid was added to it in order to set free any organic acid that might be present. An oily mass soon separated out. The supernatant liquid was poured off from the oil, and this liquid (after being allowed to stand for a number of hours) yielded yellowish crystals. The oil was an acid, as was shown by its behavior toward caustic alkalies; but it could not be purified sufficiently to determine its nature. The crystals from the liquid that had been poured off were repeatedly recrystallized from hot water, but on account of the small quantity they could not be purified sufficiently to establish their identity.

By decomposing a new portion (28 grams) of orthodiazobenzoic-acid nitrate with methyl alcohol, and neutralizing and distilling as before, the free acid was obtained in a much more satisfactory condition from the liquid remaining behind in the flask. It was found not to be volatile with water-vapor, and therefore it could not be benzoic acid. By boiling it with animal charcoal and repeatedly recrystallizing from hot water, it was obtained in large white needles, soon turning yellow. The melting-point 225°, and a blood-red coloration with ferric chloride made it seem probable that this substance is the unsymmetrical nitrosalicylic acid, the derivatives of which are described in detail by Hübner.[1] The same substance was probably obtained by Remsen and Graham[2] by the decomposition of orthodiazobenzoic acid nitrate in toluene. The small quantity of the product obtained prevented any further study of its properties than that above indicated.

2. *Orthodiazobenzoic-acid Sulphate.*

Preparation of the Diazo Compound from Anthranilic Acid.—On attempting to prepare this diazo compound as I did the salts of the other diazobenzoic acids—*viz.*, by diazotizing in dilute acid solution—I soon found that, although the amino compound dissolves readily when diazotizing, it is not an easy matter to precipitate out the diazo compound from this solution. I accordingly attempted to find a more satisfactory method. The method finally employed consisted in treating 10 grams of amino acid with about 15 cc. of concentrated sulphuric acid. After cooling in a freezing-mixture it was treated with about 100 cc. of alcohol, and then diazotized in the usual way. 10 grams of amido acid yielded in this way 17–18 grams of a beautiful white diazo compound.

Decomposition with Methyl Alcohol.—128 grams of diazo compound were decomposed with methyl alcohol, the alcohol distilled off, water added, the free acid neutralized, and the residue subjected to distillation with steam, as was described in detail in the case of the corresponding nitrate. About 35 cc. of an oil were obtained. When distilled, the thermometer passed from 200° to 246° during the process.

The acid obtained by the saponification of a portion of this oil did not have a sharp melting-point. The oil was then subjected to fractional distillation. The oil boiling from 200°–210° and that distilled from 240°–246° were saponified separately. The former yielded benzoic acid, melting at 120°; and the latter yielded methylsalicylic acid, melting at 99°.

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[1] Ber. d. chem. Ges., 8, 1217.

[2] This Journal, 11, 325.

3. *Metadiazobenzoic-acid Sulphate.*

Preparation of the Diazo Compound from Metaminobenzoic Acid.—The diazo compound was prepared according to the method of Griess,[1] except that I did not generally filter the mixture (after saturating with nitrous fumes) before precipitating out the diazo compound by means of alcohol and ether. The diazo compound was white at first, but it soon turned to a beautiful yellow. It seemed to be quite stable; a portion of it was kept over night without any apparent change. 10 grams of the metaminobenzoic acid yielded from 8-11 grams of the diazo compound, according to the conditions of the experiment.

Decomposition with Methyl Alcohol.—50 grams of the diazo compound, divided into several portions, were decomposed with methyl alcohol according to the method described in the case of the decomposition of the orthodiazobenzoic-acid nitrate. Decomposition began when the water-bath reached 60° and went forward quite rapidly. After the methyl alcohol was distilled off, water was added. The liquid in the flask arranged itself in two layers, an oil sinking below the water as in the case of the decomposition-products from the ortho compound. After distillation with steam, about 20 cc. of an oil were obtained from the distillate. Some trouble was experienced in drying this oil. On distillation, its boiling-point was found to be about 240°. The oil was saponified by boiling it with a concentrated aqueous solution of potassium hydroxide in a flask connected with an inverted condenser. The contents of the flask were diluted with water and the acid was set free by means of hydrochloric acid. The white solid was collected on a filter and freed from adhering liquid by means of a filter-pump. It was then recrystallized from boiling water. The product was an unusually beautiful one. The melting-point was found to be 106°, which agrees with that assigned to metamethoxybenzoic acid by Oppenheim and Pfaff.[2] The oil from which the acid is derived must therefore be regarded as an ethereal salt. No products other than methyl metamethoxybenzoate were obtained from the products of decomposition.

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[1] Ber. d. chem. Ges., **9**, 1655.

[2] *Ibid*, **8**, 887.

Decomposition with Ethyl Alcohol.—115 grams of diazo compound were decomposed with ethyl alcohol and the products of decomposition were treated in the same way as just outlined for the decomposition with methyl alcohol. About 30 cc. of a light-colored oil were obtained from the distillate. It boiled from 210°–211°, and, on saponification, yielded benzoic acid, which was recognized by its melting-point. This, together with the fact that aldehyde is given off during the decomposition, renders it evident that ethyl benzoate is the main product of the decomposition.

On distilling the oil carefully, however, the last few drops indicated a higher boiling-point. These were collected separately and saponified. By recrystallizing from a large excess of water (to separate from benzoic acid[1]) an acid having a melting-point of 136° was obtained, probably identical with the ethoxybenzoic acid described by Heintz.[2]

4. *Paradiazobenzoic-acid Nitrate.*

Preparation of the Diazo Compound from Paraminobenzoic Acid.—The diazo compound was prepared according to the method of Griess.[3] 10 grams of paraminobenzoic acid were treated with about 20 cc. of strong nitric acid. After cooling in ice-water, 20 cc. of dilute nitric acid were added, and the whole was shaken so as to form a pasty mixture. The flask was placed in a freezing-mixture of ice and hydrochloric acid and a rapid current of nitrous fumes was passed through the mixture until the contents of the flask went into solution. On adding to this 100 cc. of cold ether and about 75 cc. of cold alcohol, a precipitate of diazo compound was formed at once. The product was white, and in no case did I obtain it of the color of a light-brown sugar, as it is described by Remsen and Graham.[4] It was readily soluble in water and exploded when heated on platinum foil. 10 grams of aminobenzoic acid gave from 12 to 14 grams of diazo compound.

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[1] Griess: Ber. d. chem. Ges., **21**, 979.

[2] Ann. Chem. (Liebig), **153**, 334.

[3] *Ibid*, **120**, 126.

[4] This JOURNAL, **11**, 326.

Decomposition with Methyl Alcohol.—66 grams of the diazo compound, divided into several portions, were decomposed with methyl alcohol according to the method described in the case of the corresponding ortho compound. There was active decomposition when the temperature (60°) of the water-bath was reached. After the methyl alcohol was distilled off, and water added, the liquid in the flask arranged itself in two layers, an oil sinking below the water as in the case of the ortho compound. On distillation with steam for about two hours, the first product was a considerable quantity of an oil which soon turned solid. The later portions of the distillate were collected separately, and the product obtained was a white solid. Both products were found to be but sparingly soluble in water. On recrystallization, the two were found to be identical, each having the melting-point 48°—corresponding to the properties of the methyl paramethoxybenzoate described by Cahours.[1] The distillation with steam was not continued long enough to carry over all of this product.

The part remaining behind in the flask still consisted of an aqueous layer above a heavier oily liquid. The aqueous portion was separated while it was still warm, and set aside to crystallize. The crystals obtained from it were found to be impure anisic acid, but this portion was not purified, inasmuch as anisic acid was found elsewhere, as will be shown. The oily portion was poured into a distilling-bulb before it could solidify, and was subjected to distillation. A little water came over at first and then the thermometer rose rapidly to about 255°, the boiling-point of methyl paramethoxybenzoate. The portion boiling from 255°–260° was collected separately. A small portion of this distillate was saponified, and the anisic acid obtained from it was recrystallized from boiling water and its melting-point determined. The later portions of the distillate (boiling between 275° and 280°) were caught separately and a part was recrystallized from boiling water. The product was apparently not pure, so the free acid was dissolved by a solution of sodium carbonate, the solution filtered and the pure anisic acid precipitated by means of hydrochloric acid. The residue remaining behind on filtering the solution of the sodium salt was found to have the melting-point 47°, showing it to be the ethereal salt. The relative quantities of the products formed were not determined.

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[1] Ann. Chem. (Liebig), **56**, 311.

5. *Paradiazobenzoic-acid Sulphate.*

Preparation of the Diazo Compound from Paraminobenzoic Acid.—10 grams of the paraminobenzoic acid were treated with 30 cc. strong sulphuric acid, and after cooling, 60 cc. dilute sulphuric acid were added. This was cooled in a freezing-mixture, and a rapid current of nitrous fumes was passed through until the liquid became clear. The diazo compound was precipitated out promptly on the addition of ether and alcohol.

Decomposition with Methyl Alcohol.—77 grams of the diazo compound prepared as just described were decomposed with methyl alcohol in several portions as described under the orthodiazobenzoic acid. After distilling off the methyl alcohol a considerable quantity of crystals separated out from the liquid on cooling. This solid product was filtered off and was found to weigh 18 grams. Part of it was melted and distilled. Its boiling-point was determined to be about 250°. Another portion was saponified, yielding anisic acid. Still another portion was recrystallized and its melting-point was determined to be 48°. All these experiments indicate that the solid thus obtained is the methyl ether of anisic acid.

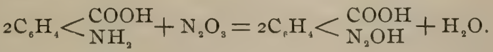
The filtrate from the crystals was subjected to distillation with steam, as the decomposition-products from the nitrate had been previously. Methyl paramethoxybenzoate (recognized by its pleasant anise-like odor and also by its melting-point) was found in the distillate. Methyl benzoate, if formed at all, is not formed in sufficient quantity to detect its presence with the quantities of material here employed. From the liquid remaining in the flask after distillation, a small quantity of an acid melting at about 177° was separated. This may have been impure anisic acid. But the free anisic acid, if formed at all in this reaction, is certainly much less in quantity than that formed with the corresponding nitrate.

Comparison of the Above Results with Those Obtained by Griess.—In an appendix to a paper on diazo compounds derived from the aromatic acids, Griess[1] says that these compounds are not formed at all when a large excess of nitrous acid is allowed to act on a hot alcoholic solution of the amido acid. Under these conditions a hydrogen atom is substituted for the amido group in the acid, nitrogen is liberated, and aldehyde and water are formed. He says: "In this way all the amido-acids that I have thus far had an opportunity to examine are converted into an acid which is identical or isomeric with that from which the amido acid is obtained by nitration and reduction of the nitro compound."

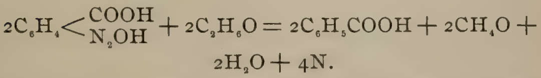
This was at a time when there was supposed to be more than one variety of benzoic acid; and Griess says that the "salylic acid" described by Kolbe and Lautemann[2] is the product obtained from amidobenzoic acid. He recommends the method above described as an admirable method for the preparation of salylic acid, the supposed isomer of benzoic acid. With the atomic weights at present used, the reactions he gives would become in the case of amidobenzoic acid:

$$2C_7H_7NO_2 + N_2O_3 + 2C_2H_6O = 2C_7H_6O_2 + 2C_2H_4O + \\ 3H_2O + 4N.$$

If we wish to indicate the formation of the diazo compound we might represent the same facts by writing the two following reactions:



$$2C_6H_4{<}\begin{matrix}COOH\\NH_2\end{matrix} + N_2O_3 = 2C_6H_4{<}\begin{matrix}COOH\\N_2OH\end{matrix} + H_2O.$$



$$2C_6H_4{<}\begin{matrix}COOH\\N_2OH\end{matrix} + 2C_2H_6O = 2C_6H_5COOH + 2CH_4O + \\ 2H_2O + 4N.$$

In a later paper[3] he describes more in detail his results in decomposing the sulphates of the three diazobenzoic acids with methyl alcohol as well as with ordinary alcohol. With methyl alcohol he obtained in the case of the ortho compound only benzoic acid, and in the case of both the meta and para compounds only methoxy acids. With ordinary alcohol he found that only the hydrogen reaction takes place in the case of the ortho compound, and both the hydrogen and ethoxy reaction, in the case of the meta and para compounds.

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[1] Ann. Chem. (Liebig), **117**, 63.

[2] *Ibid.* **115**, 187.

[3] Ber. d. chem. Ges., **21**, 979.

Fittica,[1] too, obtained the metethoxybenzoic acid from alcohol and metadiazobenzoic-acid sulphate.

With ordinary alcohol, Remsen and Graham[2] obtained ethyl benzoate as the principal product from the ortho and meta acids, and paraethoxybenzoic acid from the para acid. They also obtained the alkoxy reaction with methyl and propyl alcohols and paradiazobenzoic acids.

Excepting the formation of some methyl benzoate from orthodiazobenzoic acid sulphate, the tendency as shown by my experiments seems to be altogether toward the methoxy reaction, accompanied by a total or partial conversion of the methoxy acid into an ethereal salt. From methyl alcohol and the nitrate of orthodiazobenzoic acid under the conditions of the experiment described in this paper there is no free benzoic acid obtained. Further than this, it seems probable that the oil obtained is (as in the case of the sulphate), in part at least, an ethereal salt of the methoxy acid.

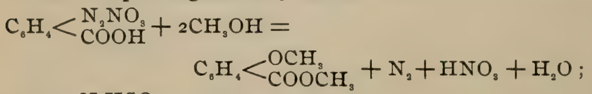
I am at a loss to explain the differences in the results obtained and shall make no attempts to reconcile them. From all the results it is however evident that methyl alcohol is more apt to give the alkoxy reaction than ordinary alcohol.

Summary.

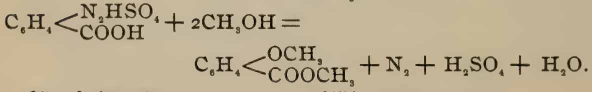
Orthonitrodiazobenzene sulphate yielded nitrobenzene as the only product of the reaction that can be isolated.

The para and metanitrodiazobenzene nitrates yielded mostly nitrobenzene, and some nitranisol.

The salts of the diazobenzoic acids all yielded as the principal product of the reaction with methyl alcohol the ethereal salts of the corresponding methoxy acids. Thus:



$$C_6H_4<\substack{N_2NO_3\\COOH} + 2CH_3OH = C_6H_4<\substack{OCH_3\\COOCH_3} + N_2 + HNO_3 + H_2O;$$



$$C_6H_4<\substack{N_2HSO_4\\COOH} + 2CH_3OH = C_6H_4<\substack{OCH_3\\COOCH_3} + N_2 + H_2SO_4 + H_2O.$$

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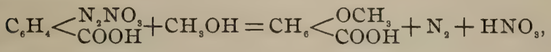
[1] Ber. d. chem. Ges., II, 1209.

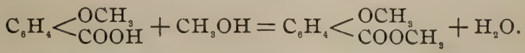
[2] This Journal, II, 325.

These processes probably take place in two steps: First, the decomposition of the diazo compound with the alcohol, yielding the corresponding methoxy acid, and then the formation of an ethereal salt by the action of the alcohol on the methoxy acid. In the case of the two nitrates the reactions would be



$$C_6H_4<\begin{matrix}N_2NO_3\\COOH\end{matrix}+CH_3OH=CH_6<\begin{matrix}OCH_3\\COOH\end{matrix}+N_2+HNO_3,$$

and

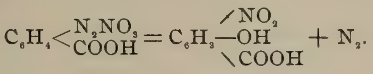


$$C_6H_4<\begin{matrix}OCH_3\\COOH\end{matrix}+CH_3OH=C_6H_4<\begin{matrix}OCH_3\\COOCH_3\end{matrix}+H_2O.$$

In the case of paradiazobenzoic acid nitrate, some of the free anisic acid was obtained.

With the *orthodiazobenzoic acid sulphate* some methyl benzoate is also formed together with the methyl methoxybenzoate, as was shown by fractional distillation of the oil and the fact that benzoic acid was obtained by saponification of the lower boiling portion.

With the *orthodiazobenzoic acid nitrate* some nitrosalicylic acid was obtained by loss of nitrogen and molecular rearrangement[1] thus:



$$C_6H_4<\begin{matrix}N_2NO_3\\COOH\end{matrix}=C_6H_3\begin{array}{l}\diagup NO_2\\-OH\\\diagdown COOH\end{array}+N_2.$$

XII.—A STUDY OF THE ACTION OF METHYL ALCOHOL ON THE SULPHATE OF ORTHODIAZOTOLUENE.[2]

By William Bromwell.

Preparation of Orthodiazotoluene Nitrate.

The method of Knoevenagel[3] for the preparation of dry diazo salts was tried as follows:

Fifteen grams of orthotoluidine nitrate were dissolved in about 350 cc. of alcohol and the solution acidified with a few drops of nitric acid and cooled to 0°. 12.5 grams of amyl nitrite were now added slowly while stirring. After standing about fifteen minutes, ether was added to aid the separation of the diazo compound. This experiment was repeated several times, but in no case could the diazo nitrate be obtained in this way, except in very small quantities. It was apparently decomposed as fast as formed, even though the temperature was kept at 0°. The solution became very dark and there was an evolution of nitrogen. The best yield was obtained by passing nitrous fumes, derived from the action of nitric acid upon arsenic, through the orthotoluidine nitrate mixed to a thin paste with alcohol, and kept cold by a freezing-mixture. After a time the salt went into solution, and finally a test with dilute caustic soda did not give the odor of toluidine. The action was then complete, and the solution was poured into strong alcohol (from lime), and ether slowly added with constant stirring till a permanent cloudiness resulted. As soon as the precipitation of the diazo compound commenced, more ether was added until no further precipitation was caused. The mixture was then allowed to stand for several hours, when the precipitate assumed a crystalline character, and was much more easily washed than when freshly precipitated, when it is usually somewhat gummy. It was then drained as completely as possible from the mother-liquor with the aid of the pump, and washed several times with cold absolute alcohol, and then with ether until the washings were colorless. The ether was then sucked off as completely as possible, and the crystals spread upon a porous plate to dry. When first washed with ether they were very light brown, but rapidly darkened upon exposure on a plate.

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[1] Remsen and Orndorff: This Journal, **9**, 396.

[2] From the Author's Thesis, submitted to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy, June, 1895.

[3] Ber. d. chem. Ges., **23**, 2994.

The first time the nitrate was prepared for this investigation, it remained on the plate for about twenty-four hours, when it became very dark and moist. On close examination it was found to be studded with minute fine yellow needles, and smelled strongly of cresol. While preparing to pick out some of these needles to determine their melting-point, the whole mass (about 38 grams) decomposed with violent explosion. The only apparent cause for the explosion was the heat from a Bunsen burner, which was burning at a distance of about twenty inches from the plate. The temperature could not have been raised more than a very few degrees.

A second lot of the nitrate (approximately 40 grams) was prepared in exactly the same way, and to avoid the possibility of an explosion care was taken to see that no flame was within ten feet of it. However, on taking it from the funnel and spreading it upon the porous plate to remove the last traces of ether, it immediately exploded with terrific violence, without any apparent cause. The force of the explosion was so great that the top of the table was badly shattered. All the gas burners in the room were extinguished, and the noise was so great that some of the men working in the room were temporarily deafened. The author's hand was injured to such an extent that it could not be used for about six weeks. As the nitrate was so unstable, upon resumption of work, the investigation was confined for the present to the sulphate.

Preparation of Orthodiazotoluene Sulphate.

The preparation of orthodiazotoluene sulphate is much more easily accomplished than that of the corresponding nitrate. The Knoevenagel method, that involving the use of amyl nitrite, was tried, and found to be very satisfactory, but the results were not materially better than those obtained by the use of the nitrous fumes from arsenic and nitric acid. The former is slightly quicker, but the presence of the amyl alcohol makes the recovery of the ordinary alcohol and ether more difficult. Therefore the following method, that used by Remsen and Orndorff[1] for this compound, and by Chamberlin[2] for the corresponding para compound, was adopted.

25 grams of pure orthotoluidine are dissolved in 250 cc. of ordinary alcohol in an Erlenmeyer flask, and a slight excess (25 grams) of sulphuric acid carefully added, drop by drop, with constant shaking until the orthotoluidine sulphate thus formed has dissolved. The flask is now placed in ice-water, and the fumes from nitric acid and arsenic, after passing through two wash-bottles immersed in ice-water, are conducted into the solution until the reaction is complete. This usually requires from one to two hours. The end of the reac-

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[1] This JOURNAL, 9, 394.

[2] See preceding article.

tion is best recognized by the appearance of the crystalline precipitate. The crystals of orthodiazotoluene sulphate are fine well-characterized needles, which are heavier than the irregular, flaky crystals of orthotoluidine sulphate. The action of the nitrous fumes is then stopped, the crystals filtered off, and to the filtrate ether is added when, after standing in an ice-bath for several hours, a second crop of crystals is obtained. The crystals are first washed with ordinary alcohol, and then with absolute alcohol till the washings are colorless. The alcohol is then washed out with anhydrous ether, which is sucked off as completely as possible with the pump. The salt is then spread out on a porous plate, and the last traces of ether rapidly disappear. Sometimes the salt has a bluish-green color; at others it is nearly white, turning pink on washing with alcohol. Exposed to the air on a porous plate at ordinary temperatures the salt is comparatively stable, no signs of explosion having been noticed, and only slight changes in color taking place in twenty-four hours.

The *methyl alcohol* used in these experiments was that sold as "Columbian Spirit," and obtained from H. C. Collier, Binghampton, N. Y. It was examined together with the best German methyl alcohol, and was found to compare very favorably with this, having slightly less of the empyreumatic odor. The German alcohol contained slightly less water than the "Columbian Spirit," but the following experiments show that there is little difference between them:

250 cc. each of the two kinds of methyl alcohol were treated with lime for eighteen hours and then distilled.

The German sample began to distil at 64°, and the temperature immediately rose to 65°.2, and remained at about 65° until all but the last few drops had come over. The "Columbian Spirit" started at 64° and rose steadily to 66°.

Now 50 cc. each of these distillates were redistilled. The German sample in this case distilled between 64°.5 and 65°, while the "Columbian Spirit" ranged from 64° to 66°, and just as the last few drops went off the temperature rose to 68°.

These experiments indicate that there was a little more water in the American specimen. Therefore the prolonged action of lime was tried, and it was found that, after standing for forty-eight hours, nearly all of a 750 cc. sample boiled exactly at 65° with a Hempel distilling-tube.

As this was perfectly satisfactory, the alcohol used in the following experiments was all prepared in this way from the "Columbian Spirit," the cost of which is just about one-fourth that of the imported article.

Action of Methyl Alcohol on Orthodiazotoluene Sulphate.

1. *At the Ordinary Room Temperature.*—About 30 grams of dry orthodiazotoluene sulphate were placed in a long-necked balloon-flask of about two liters' capacity, and treated with 100 cc. of methyl alcohol (from lime). The flask provided with a return-condenser was allowed to remain at the room temperature (about 20°). The action commenced at once, and there was quite a brisk evolution of nitrogen, but no perceptible odor of aldehyde. If the flask is left undisturbed the action is completed in about twenty hours, but it can be materially hastened by frequent shaking. It was then boiled on the water-bath for a short time to insure complete decomposition.

350 grams of orthodiazotoluene sulphate in portions of 30–40 grams were decomposed in this way with about 1400 cc. of methyl alcohol. The various portions were united and the alcohol distilled off on the water-bath. This distillate was added to about five times its volume of a saturated solution of common salt, when an oil of a pale yellow color slowly separated and rose to the surface. Water was then added to the residue remaining in the flask, and the distillation continued with steam. A yellow oil distilled over with the water. Its specific gravity is very nearly that of water. The residue in the flask consisted of a clear liquid and a black tarry substance, which later became quite hard and brittle upon cooling. The temperature was reduced to 0°, and the liquid filtered off and evaporated. Nothing except sulphuric acid was found in the residue. The tar, a black, solid mass, was extracted with alcohol, and most of it went into solution, but nothing was obtained from it.

The oils were then washed and dried over calcium chloride. They both have the same pleasant, aromatic odor, suggesting that of the oil of wintergreen, but still quite different from it.

35 grams of the oil were obtained in this way from the alcoholic distillate. On distilling this, only a few drops came over as the thermometer went steadily up to 160°, nearly all coming over between 164° and 174°, only about 1 gram being left in the flask at 174°.

97 grams of the oil were obtained from the steam distillate; 73 grams came over between 164° and 170°; and most of the rest between 170° and 174°, leaving as above, only about 1 gram in the flask. These two portions of oil, boiling between 164° and 174°, being apparently identical, were united and set aside.

2. *At a Temperature near that of the Boiling-Point of the Alcohol.*—400 grams of the orthodiazotoluene sulphate were decomposed by heating the flask, provided with a return-condenser and containing about 30 grams of the salt and about 100 cc. of absolute methyl alcohol, on the water-bath at about 50°–60° for about half an hour, when the action was apparently complete. The contents of the flask were then boiled for a few minutes to insure complete decomposition. The various portions decomposed in this way were united, and were treated exactly as in the preceding experiment. The alcohol was distilled off, and 46 grams of oil were obtained from the alcoholic distillate on treatment with a strong solution of common salt.

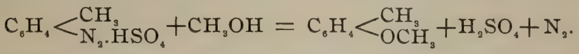
The distillation was then continued with steam, and 115 grams of the oil were thus obtained.

The oil obtained from the alcoholic distillate was washed, dried, and distilled, nearly all of it coming over between 164° and 174°.

The oil from the steam distillate was then treated in the same way, and nearly all of it came over between the same points, only about 5 grams coming over below 160° and about 12 grams above 174°, from both the portions.

The oil from all the various portions was then brought together and fractionated, and it was found that of the 293 grams of oil obtained altogether, 247 grams (over 84 per cent.) distilled between 167° and 170°. The average boiling-point of this portion, (168°.5) corrected for the column of mercury outside of the vapor of the oil, is 171°.35.

The boiling-point of the methyl ether of orthocresol, $C_6H_4 < \begin{matrix}CH_3\\OCH_3\end{matrix}$, as given by Pinnette[1] is 171°.3. Thus it will be seen that the principal action of methyl alcohol on orthodiazotoluene sulphate is expressed by the following equation:



$$C_6H_4<\begin{matrix}CH_3\\N_2.HSO_4\end{matrix}+CH_3OH = C_6H_4<\begin{matrix}CH_3\\OCH_3\end{matrix}+H_2SO_4+N_2.$$

This corresponds to the decomposition of the same diazo salt with ordinary alcohol, as observed by Remsen and Orndorff,[2] who obtained as the chief product the ethyl ether of orthocresol. If toluene was formed, it was in such small quantities as to escape their notice. In these experiments, however, in which larger quantities were used, there was enough of the oil boiling below 130° to enable us to prove the presence of toluene. This was done by adding a few drops of the oil to hot fuming nitric acid and pouring the mixture into water. On standing, crystals separated out which melt at 55°, and are, therefore, paranitrotoluene. No odor of formic aldehyde was observed during any of the decompositions. Apparently there was slightly more of the low-boiling oil formed in the second experiment where the decomposition was effected at the higher temperature, though the difference was so slight, and the quantities of toluene so small in both cases that no conclusion of value could be drawn.

Orthomethoxytoluene, or the Methyl Ether of Orthocresol.

The methyl ether of orthocresol was made by Pinnette[3] from phenol, potassium hydroxide, and methyl iodide, according to the Williamson reaction, and is described by him only as boiling at 171°.3, and as having the specific gravity 0.9957 at 0°. In consideration of the fact that this is the only knowledge we have of the substance, it was thought well to study it a little further. It is a colorless, very highly refracting, mobile oil, with a rather pleasant, aromatic odor, as above described, suggesting the oil of wintergreen, though differing

[1] Ann. Chem. (Liebig), **243**, 37.

[2] Am. Chem. J., **9**, 387.

[3] Ann. Chem. (Liebig), **243**, 37.

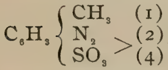
markedly from it. It is almost insoluble in water, but easily soluble in alcohol and ether.

Action of Sulphuric Acid on Orthomethoxytoluene.

Forty grams of orthomethoxytoluene were poured slowly into 120 grams of concentrated sulphuric acid. Action took place at once, the oil going into solution with the formation of a decided rose color. The mixture was shaken for a few minutes to insure complete reaction, and it was then poured into about a liter and a half of water, and neutralized with barium carbonate. The salt thus obtained was recrystallized, and the appearance of the crystals, which were small, transparent, glistening plates, and also still smaller white granules, suggested the possibility of two sulphonic acids.

Therefore, the salt was subjected to careful and prolonged fractional crystallization. Specimens of the salts from the extremes and from the middle of the series of fractions were taken, and from these were made first the sodium salts. These were treated with phosphorus pentachloride, and the sulphone chlorides obtained. These were solid and were apparently all the same. They were now treated with ammonia, and the amides were thus made and recrystallized. All three amides melt sharply at 137°, and are therefore derived from the same sulphonic acid. This in turn shows that the result of treating the methyl ether of orthocresol is beyond doubt only one sulphonic acid. As this acid has not been described in the literature, it was decided to make and study some of its salts and derivatives.

Hayduck[1] decomposed the diazo compound of the formula,



$C_6H_3\left\{\begin{array}{lll} CH_3 & & (1)\\ N_2 & > & (2)\\ SO_3 & & (4)\end{array}\right.$, with methyl alcohol, and obtained orthomethoxyparatoluenesulphonic acid, the barium salt of which he describes as crystallizing in small shining plates with two molecules of water of crystallization, which it does not lose over sulphuric acid.

The barium salt to be presently described as made from orthomethoxytoluene by treatment with sulphuric acid and neutralizing with barium carbonate, agrees closely with that made by Hayduck. The latter, as above mentioned, crystallized in whitish, irregular crystals mixed with shining transparent plates. In the course of fractional crystallization it is observed that it depends largely on the concentration of the solution which kind of crystals predominates. If the solution is comparatively weak, the crystals are nearly all shining plates; but if the solution is quite concentrated the white opaque crystals are the rule. In a sample of the shining plates the water of crystallization was determined and found to correspond closely to the formula

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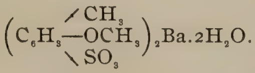
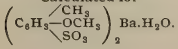
[1] Ann. Chem. (Liebig), 172, 217.



$$\left(C_6H_3\begin{matrix}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3\end{matrix}\right)_2Ba.2H_2O.$$

Calculated 6.26 Found 6.18

In another sample of the opaque variety the water and barium were estimated with the following results:

	Calculated for  $\left(C_6H_3\begin{matrix}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3\end{matrix}\right)_2Ba.H_2O.$	Found.
H_2O	3.23	3.83
Ba	24.43	24.37

It will thus be seen that the salt crystallizes sometimes with one and sometimes with two molecules of water of crystallization. It is also almost impossible to obtain a crop of crystals entirely of either form. For this reason the analyses do not give especially good results.

Remsen and Parks[1] noted a similar influence of the concentration of the solution on the crystallization of the barium salt of paramethoxyorthotoluenesulphonic acid.

Orthomethoxytoluenesulphonic Acid.—As it seemed desirable to make a further study of this acid and its salts, some of the free acid was prepared by exactly neutralizing a solution of the barium salt with dilute sulphuric acid. The barium sulphate was filtered off, and the filtrate evaporated to a small bulk. The acid is very soluble in water, and in order to make it crystallize a few drops of a saturated solution of common salt were added as recommended by Gattermann,[1] whereupon crystallization immediately commenced with the formation of beautiful, stellate clusters of short needles throughout the whole solution. The acid is filtered off, and, when dried, found to melt at 212°.

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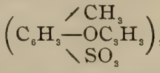
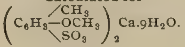
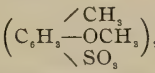
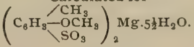
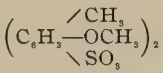
[1] This JOURNAL, **15**, 320.

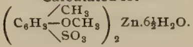
Calcium Salt,  $\left(C_6H_3\begin{matrix}/CH_3\\ -OC_3H_3\\ \backslash SO_3\end{matrix}\right)_2Ca.9H_2O$. — This salt is very soluble in water and slightly less so in alcohol. From water it crystallizes in large, colorless, transparent plates, which are very efflorescent. Analyses for water and calcium gave the following results:

	Calculated for  $\left(C_6H_3\begin{matrix}/CH_3\\ -OCH_3\\ \backslash SO_3\end{matrix}\right)_2Ca.9H_2O$.	Found. I.	II.
H_2O	26.82	26.82	26.51
Ca	6.62	6.60	6.68

Magnesium Salt,  $\left(C_6H_3\begin{matrix}/CH_3\\ -OCH_3\\ \backslash SO_3\end{matrix}\right)_2Mg.5\frac{1}{2}H_2O$.—This salt is easily soluble in water, but crystallizes well from it in large, well-developed, colorless, transparent prisms, which are not changed by exposure to the air. Analyses for water and magnesium gave the following results:

	Calculated for  $\left(C_6H_3\begin{matrix}/CH_3\\ -OCH_3\\ \backslash SO_3\end{matrix}\right)_2Mg.5\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	18.85	19.11	19.03
Mg	4.57	4.56	4.42

Zinc Salt,  $\left(C_6H_3\begin{matrix}/CH_3\\ -OCH_3\\ \backslash SO_3\end{matrix}\right)_2Zn.6\frac{1}{2}H_2O$.—This salt crystallizes from water, in which it is easily soluble, in large, colorless, transparent rectangular plates, which lose part of their water on exposure to the air. Analyses for water and zinc gave the following results:

	Calculated for  $\left(C_6H_3\begin{matrix}/CH_3\\ -OCH_3\\ \backslash SO_3\end{matrix}\right)_2Zn.6\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	20.03	19.42	19.84
Zn	11.13	10.70	10.98

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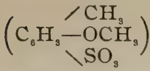
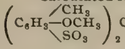
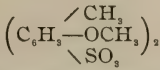
[1] Ber. d. chem. Ges., **24**, 2121.



Copper Salt, $\left(C_6H_3\begin{matrix}/CH_3\\-OCH_3\\\backslash SO_3\end{matrix}\right)_2 Cu.6H_2O$.—The crystals are small, transparent, apple-green prisms, many of which have an apparently hexagonal section. They are easily soluble in water and are quite stable in the air. Analyses for water and copper gave the following results :

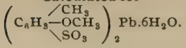


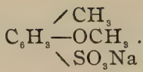
	Calculated for $\left(C_6H_3\begin{matrix}/CH_3\\-OCH_3\\\backslash SO_3\end{matrix}\right)_2 Cu.6H_2O$.	Found. I.	II.
H_2O	18.85	18.62	18.52
Cu	10.99	10.74	10.64

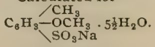


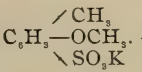
Lead Salt, $\left(C_6H_3\begin{matrix}/CH_3\\-OCH_3\\\backslash SO_3\end{matrix}\right)_2 Pb.6H_2O$. — This salt crystallizes from its water solution in thin leaflets with a pearly luster. These lose water, and with it their luster, on exposure to the air. This salt is quite unstable, decomposing within a few degrees of the point at which it ceases to give off water of crystallization, *i. e.*, approximately at 115°.

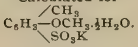
Much difficulty was experienced in the analysis of this salt both for the water, on account of the above-mentioned fact, and also for the lead, because of the ease with which lead sulphate is reduced. The analysis was most satisfactorily made in the following manner: The salt is weighed into a porcelain crucible and heated in the air-bath to about 110° to constant weight. It is now treated with a drop of sulphuric acid and one or two drops of nitric acid and heated carefully. When dry, more nitric acid is added as needed to oxidize the carbon. When this is accomplished a few drops of aqua regia are added and the crucible *very* gently heated for some time. Then sulphuric acid is added and evaporated repeatedly at as low a temperature as possible. It is finally brought to a dull red heat, until the free sulphuric acid has all been driven off. It is then cooled and weighed. The results were low in every case, and only by working with the utmost care, as above described, could approximate results be obtained.

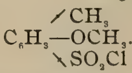
	Calculated for  $\left(C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3\end{array}\right)_2 Pb.6H_2O.$	Found.
H_2O	15.06	15.50
Pb	28.77	28.54

Sodium Salt,  $C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3Na\end{array}$. $5\frac{1}{2}H_2O$. — This salt crystallizes in large colorless, transparent needles, which rapidly lose water on exposure to the air. Analyses for water and sodium gave the following results:

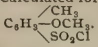
	Calculated for  $C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3Na\end{array} . 5\frac{1}{2}H_2O.$	Found. I.	Found. II.
H_2O	30.65	29.53	29.22
Na	10.27	10.21	10.89

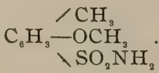
Potassium Salt,  $C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3K\end{array}$. $\frac{1}{2}H_2O$.—This is so very easily soluble in water that it was found to be impossible to obtain it well crystallized from that solvent. It is much less easily soluble in alcohol, and from this it is obtained under certain conditions, in small, transparent, rhombic plates. Analyses for water and potassium gave the following results:

	Calculated for  $C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_3K\end{array} . \frac{1}{2}H_2O.$	Found.
H_2O	3.61	3.91
K	16.25	16.31

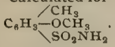
Orthomethoxytoluenesulphone Chloride,  $C_6H_3\begin{array}{l}\diagup CH_3\\ -OCH_3\\ \diagdown SO_2Cl\end{array}$. — The sodium salt was thoroughly dried in the air-bath at 120° and powdered. After cooling it was treated with a slight excess of phosphorus pentachloride. Action was brought about by rubbing the two together in a dry evaporating-dish with a dry pestle. Action took place quite readily, and after it was over and the mixture had cooled, cold water was added, when the chloride, which was at first soft, became quite hard and brittle, so that it was easily powdered and washed. A part of this was now dissolved in ether, from which it solidified in a compact, white, crystalline mass.

An estimation of chlorine gave the following result:

	Calculated for  $C_6H_3\begin{array}{l} \diagup CH_3 \\ -OCH_3 \\ \diagdown SO_2Cl \end{array}$.	Found.
Cl	16.78	16.34

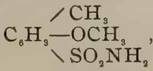
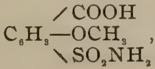
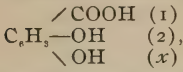
Orthomethoxytoluenesulphonamide,  $C_6H_3\begin{array}{l} \diagup CH_3 \\ -OCH_3 \\ \diagdown SO_2NH_2 \end{array}$. — This was made by treating the sulphone chloride, which has just been described, with ammonia, and allowing the mixture to stand for several hours. Most of the ammonia was now evaporated off, as the sulphonamide was found to be somewhat soluble in it. On cooling, the crystals were separated from the mother-liquor, and recrystallized from hot water.

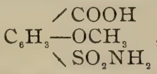
As thus obtained, they are beautiful, fine, white needles, which melt at 137°. Analyses gave the following results:

	Calculated for  $C_6H_3\begin{array}{l} \diagup CH_3 \\ -OCH_3 \\ \diagdown SO_2NH_2 \end{array}$.		Found.	
		I.	II.	III.
N	6.98	7.13	7.18	7.04
C	47.73	47.69	...	...
H	5.64	5.43	...	...

The figures under I. for nitrogen, carbon, and hydrogen, were kindly furnished by Mr. C. D. Ragland. The nitrogen in this, as in the second case by Messrs. J. W. Lawson and E. S. Smith, was estimated by the Dumas method. The third estimation of nitrogen, furnished by Mr. Lawson, was made by the Kjeldahl method.

Constitution of Orthomethoxytoluenesulphonic Acid. — From a study of the compound, it was seen that when orthomethoxytoluene is treated with sulphuric acid only one acid residue enters into the compound.

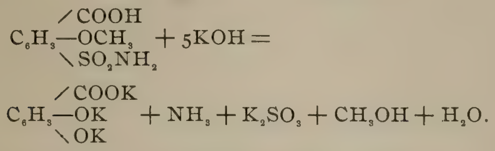
In order to determine the position of the sulphonic acid residue, it was thought that it would be easy to pass from the sulphonamide,  $C_6H_3\begin{array}{l} \diagup CH_3 \\ -OCH_3 \\ \diagdown SO_2NH_2 \end{array}$, to orthomethoxysulphaminebenzoic acid,  $C_6H_3\begin{array}{l} \diagup COOH \\ -OCH_3 \\ \diagdown SO_2NH_2 \end{array}$, by oxidation with potassium permanganate; and from this, by fusion with potassium hydroxide, to one of the four possible dihydroxybenzoic acids,  $C_6H_3\begin{cases}COOH & (1)\\ OH & (2)\\ OH & (x)\end{cases}$, which are known. To accomplish this the following experiments were performed:

Formation of Orthomethoxysulphaminebenzoic Acid.—Ten grams of the sulphonamide, as formed above, were treated with 34 grams of potassium permanganate in about a liter of water. These were heated in a balloon-flask with a return-condenser from eight to ten hours, when the permanganate was completely reduced. In case this should not be so, a few drops of alcohol may be added to complete the reduction. The oxides of manganese were now filtered off, and the solution containing the potassium salt of the acid was evaporated to a small volume. It was then acidified with hydrochloric acid, when the free acid,  $C_6H_3\begin{cases}COOH\\ OCH_3\\ SO_2NH_2\end{cases}$, crystallized out. This was filtered off and dissolved in a dilute solution of sodium carbonate to separate it from any amide which remained unoxidized. It was filtered, reprecipitated with hydrochloric acid, again filtered, recrystallized, and analyzed for sulphur and nitrogen with the following results:

	Calculated.	Found.
S	13.81	13.85
N	6.06	6.67

The melting-point is 211°.

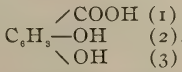
Formation of Dihydroxybenzoic Acid.—To about 10–12 grams of potassium hydroxide, in a silver crucible, a few drops of water were added. Heat was then gently applied, and the sulphaminebenzoic acid was added gradually. Care was taken to keep the temperature as little above the melting-point of the mixture as possible during the reaction, in order to avoid breaking up the carboxyl group with the elimination of carbon dioxide. The mixture was heated until a few drops of it, dissolved in a little water, gave off sulphur dioxide when treated with hydrochloric acid. The mass was then allowed to cool, dissolved in water and acidified. It was then evaporated to crystallization, cooled, filtered. When recrystallized the product appeared either as moderately large needles or as very small, short prisms. The changes which were expected here arerepresented by the equation :



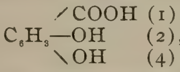
$$C_6H_3\begin{array}{l}\diagup COOH\\ -OCH_3\\ \diagdown SO_2NH_2\end{array} + 5KOH = C_6H_3\begin{array}{l}\diagup COOK\\ -OK\\ \diagdown OK\end{array} + NH_3 + K_2SO_3 + CH_3OH + H_2O.$$

The substance thus obtained was well crystallized and melted fairly well at about 230° with evolution of gas. A drop of a solution of ferric chloride added to a very dilute aqueous solution of the compound gave a deep red color. It did not reduce Fehling's solution.

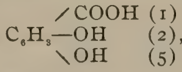
Now upon studying the four known dihydroxybenzoic acids, with one of which it might be possible for this to be identical, we find that their characteristic properties are as here given:



The 1, 2, 3 acid,[1] $C_6H_3\begin{array}{l}\diagup COOH\ (1)\\ -OH\quad (2)\\ \diagdown OH\quad (3)\end{array}$, melts at 204° and is colored dark blue by a solution of ferric chloride. It crystallizes in "water-free warts" or in needles with two molecules of water.



β-Resorcylic acid, the unsymmetrical metadihydroxybenzoic acid,[2] $C_6H_3\begin{array}{l}\diagup COOH\ (1)\\ -OH\quad (2)\\ \diagdown OH\quad (4)\end{array}$, when free from water, melts according to different observers, at 194°, 197°, 194°–200°, 204°–206°, and 213°. It is described as crystallizing with $\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, and 3 molecules of water according to circumstances. It does not reduce Fehling's solution. When heated above its melting-point it loses carbon dioxide and is converted into resorcin.



Oxysalicylic acid, $C_6H_3\begin{array}{l}\diagup COOH\ (1)\\ -OH\quad (2)\\ \diagdown OH\quad (5)\end{array}$, melts according to various authorities, at 196°–197°, or 199°–200°. Ferric chloride colors its solution deep blue. It reduces Fehling's solution.

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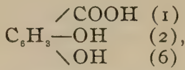
[1] Ann. Chem. (Liebig), **220**, 116.

[2] Ann. Chem. (Liebig), **161**, 11; This JOURNAL, **2**, 169; Ber. d. chem. Ges., **18**, 1985.

The acid,  $C_6H_3\begin{array}{l}\diagup COOH\ (1)\\ —OH\ \ (2)\\ \diagdown OH\ \ (6)\end{array}$, is described by Senhofer and Brunner.[1] It melts from 148°–167°. Its solution is colored violet by ferric chloride, and it reduces Fehling's solution.

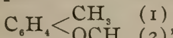
All of these acids give off carbon dioxide, forming the corresponding dihydroxy derivative of benzene.

It will be observed that the compound obtained by fusing orthomethoxysulphaminebenzoic acid with potassium hydroxide does not correspond to any of these acids. It agrees with β-resorcylic acid (1, 2, 4) in being colored red by ferric chloride, and in not reducing Fehling's solution. But its melting-point is too high, and it does not form fluoresceïn when heated with phthalic anhydride. It is suspected that the substance is not pure, and qualitative tests for sulphur and nitrogen show the presence of both. This indicates that the fusion with potassium hydroxide was not complete. Therefore, what remained of the substance was again fused with potassium hydroxide. This time the temperature was raised somewhat higher than before, and the fusion continued for about ten minutes. The mass, on cooling, became yellowish-brown. This was dissolved in water, evaporated and extracted with ether. The residue consisted of a crystalline crust on the beaker, which was studded with fine, white needles. The former melted at about 130° and the latter at 155°. Both portions were carefully tested with phthalic anhydride for resorcin, but no trace of fluoresceïn was formed. With ferric chloride the color was exactly that given by salicylic acid, and not that given by resorcin. In order to separate the acid from the dihydroxybenzene, in case they should both be present, the substance was treated with a solution of sodium carbonate, and then extracted with ether, which would take the dihydroxy derivative and leave the sodium salt of the acid in the water. The ether extract was evaporated, leaving a small impure residue which melts through a range of 15°, from 120°–135°.

[1] Wiener Akademieber., (1879), 80.

The ferric chloride color reaction was exactly that of salicylic acid. It is difficult to account for any salicylic acid here.

The small amount of material and the lack of time makes a further study of this question impossible at this time.[1]

Oxidation of Orthomethoxytoluene.—In order to furnish additional evidence that the formula of the oil obtained by the decomposition of orthodiazotoluene sulphate by methyl alcohol is  $C_6H_4<\begin{matrix} CH_3 & (1) \\ OCH_3 & (2) \end{matrix}$, some of the oil was oxidized as follows:

Thirteen grams of potassium permanganate were dissolved in about 700 cc. of water in a flask fitted with a return-condenser, and 5 grams of the oil were added. The mixture was heated on the water-bath, with frequent shaking, for about three hours, when the reduction of the permanganate was complete. The oxides of manganese were filtered off and the clear solution evaporated to about 100 cc. This was then acidified with hydrochloric acid. On cooling, beautiful, fern-like crystals separate. After recrystallization these melt at 98°.5–99°, thus agreeing closely with orthomethoxybenzoic acid, which is described by Cahours[2] as melting at 98°.

Conclusions.

This investigation shows:

1. That orthodiazotoluene sulphate is decomposed by methyl alcohol at a lower temperature than the corresponding para compound.
2. That orthodiazotoluene sulphate, when decomposed by methyl alcohol under atmospheric pressure, gives almost exclusively the alkoxy reaction.
3. That, whether the decomposition takes place slowly at the temperature of the room, or rapidly at a temperature near the boiling-point of the alcohol, the yield of the methoxy product is practically the same.
4. That when orthomethoxytoluene is treated with cold concentrated sulphuric acid only one sulphonic acid is formed.
5. That the sulphonic acid so formed is a monobasic acid containing only one sulphuric acid residue.
6. That by oxidation, orthomethoxytoluene yields orthomethoxybenzoic acid.

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[1] See the following article.—I. R.

[2] Ann. Chem. (Liebig), **42**, 60; *Ibid*, **92**, 315.

ON THE ACTION OF POTASSIUM HYDROXIDE ON ORTHOMETHOXYSULPHAMINEBENZOIC ACID.

By Charles Walker.

In the preceding article, by Mr. Bromwell, an experiment is described, the results of which are not clear. In order to determine the constitution of the sulphonic acid formed by the action of sulphuric acid on orthomethoxytoluene the acid was converted into the corresponding amide, and this oxidized. The sulphaminebenzoic acid thus obtained,

$$C_6H_3\left\{\begin{array}{l}COOH\\OCH_3\\SO_2NH_2\end{array}\right.,$$

was then fused with potassium hydroxide in the expectation that it would be converted into the corresponding dihydroxybenzoic acid. The product was, however, shown not to be a dihydroxybenzoic acid, and the investigation was not carried any farther. At this point I took it up at the suggestion of Professor Remsen, and the results are here communicated.

From 10 to 13 grams of caustic potash were placed in a silver crucible with a little water, and, after heating gently, 3 grams of the acid were added. The fusion was continued at low redness for from five to eight minutes, the mass cooled and dissolved in water. On acidifying, a white crystalline precipitate was obtained. After crystallizing from water a number of times it was analyzed.

I. 0.2145 gram substance gave 0.3021 gram CO_2 and 0.0694 gram water.

II. 0.2522 gram substance gave 0.3569 gram CO_2 and 0.0772 gram water.

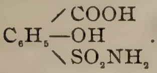
III. 0.2066 gram substance gave 12.3 cc. nitrogen at 758 mm. and 25°.

IV. 0.2452 gram substance gave 16.6 cc. nitrogen at 759 mm. and 30°.

V. 0.1740 gram substance gave 0.1901 gram $BaSO_4$.

	Calculated for $C_7H_7NSO_5$.	Found.				
		I.	II.	III.	IV.	V.
C	38.71	38.41	38.59	....	....	....
H	3.22	3.59	3.40	....	....	....
N	6.45	....	....	6.79	6.66	....
S	14.75	....	....	....	....	15.00

The combustions were made with a mixture of potassium dichromate and lead chromate.

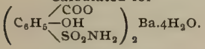
The substance, therefore, is orthoxysulphaminebenzoic acid,  $C_6H_5\begin{cases}COOH\\OH\\SO_2NH_2\end{cases}$. It crystallizes from water in white needles, which melt at 231° with decomposition. In aqueous solution with ferric chloride it gives a red coloration.

The great stability of the sulphamide group in this compound is worthy of special note. Another case of the same kind has since been brought to light in this laboratory.

Barium Salt.—The barium salt was prepared by treating the acid suspended in water with pure and finely divided barium carbonate. It crystallizes from water in aggregates of crystals of fine, white needles. After drying in the air it was analyzed.

0.9031 gram of the salt heated 15 hours at 150°–160° lost 0.1040 gram.

0.2620 gram of the anhydrous salt gave 0.1070 gram $BaSO_4$.

Calculated for  $\left(C_6H_5\begin{cases}COO\\OH\\SO_2NH_2\end{cases}\right)_2Ba.4H_2O.$	Found.
11.23	11.51
25.08	24.01

Calcium Salt.—This was prepared from Iceland spar in the same way as the barium salt. It crystallizes from aqueous solution in long fibrous needles. The water of crystallization and calcium were determined with the following results:

1.3090 grams heated fourteen hours, at 120°–125°, lost 0.2487 gram.

0.5435 gram anhydrous salt gave 0.1515 gram $CuSO_4$.

	Calculated for $(C_7H_6NSO_5)_2Ca + 6H_2O$.	Found.
H_2O	18.62	18.99
Ca	8.48	8.20

Sodium Salt.—The sodium salt was made from the barium salt by adding the calculated amount of sodium carbonate to the aqueous solution of the barium salt. It separates from aqueous solution in short, white needles. Determinations of water of crystallization and sodium were made with the following results :

1.5088 grams heated 15 hours at 160°–170° lost 0.1603 gram.

0.2247 gram anhydrous salt gave 0.0946 gram Na_2SO_4.

	Calculated for $C_7H_6NaNSO_5 + 1\frac{1}{2}H_2O$.	Found.
H_2O	10.16	10.63
Na	9.62	9.48

Silver Salt.—The silver salt was prepared in the usual manner, from the neutral ammonium salt. It separates from water solution at first as a white, non-crystalline compound, later in needles. After crystallizing a number of times it was analyzed.

0.2106 gram of the salt, dried at 110°, gave 0.0708 gram Ag.

Calculated for $C_7H_6AgSO_5$.	Found.
33.33	33.61

If the salt is heated, it begins to turn brown at 220°, becomes darker as the temperature is raised, and slowly decomposes without melting.

The fusion of orthomethoxysulphaminebenzoic acid with caustic potash, giving no clue to the position of the sulphamine group, the action of hydrochloric acid upon it was next studied. 0.7 gram was heated with 8–10 cc. of strong hydrochloric acid in a sealed tube at 150°–160° for three hours. On opening the tube considerable pressure was observed and the solution contained large, needle-shaped crystals. The hydrochloric acid was evaporated off, the solution extracted with ether, and the ether dried with calcic chloride. On evaporating off the ether, crystals of pure salicylic acid were obtained, as shown by their melting-point, form of crystals, and coloration with ferric chloride.

JOHNS HOPKINS UNIVERSITY,
June, 1896.

A SIMPLE AND EFFICIENT BOILING-POINT APPARATUS FOR USE WITH LOW- AND WITH HIGH-BOILING SOLVENTS.

BY HARRY C. JONES.

The best methods that have thus far been devised for determining the rise in the boiling-point of a solvent, caused by the presence of a dissolved substance, are not free from objections, both theoretical and practical. Some of these, apparently, cannot be eliminated, while others can be overcome to a greater or less extent.

The boiling-point method is not capable of that degree of accuracy to which the freezing-point method has been developed by Loomis[1] and myself,[2] for several reasons. Some of these have been pointed out with admirable clearness by Hite.[3] The boiling method is very sensitive to barometric changes. In this method the vapor escapes quickly from the solution in which its presence is necessary to establish the temperature equilibrium.

To these the following should be added: The difference in temperature between the liquid and surrounding objects is generally much greater in this method than in the freezing-point method, so that greater precautions are necessary to protect the solution and thermometer from changes in the temperature of external objects. In this method a part of the comparatively pure solvent is constantly separating from the solution as vapor, and is returned as a liquid, at a temperature much lower than that of the boiling solution. The amount of this liquid cannot, for given conditions, be determined with the same degree of accuracy as was possible in ascertaining the amount of ice which separated in the freezing liquid.[4] It is well known that the large Beckmann thermometers are much more liable to undergo change at the comparatively high temperatures to which it is necessary to subject them in this method, than in the freezing method, where the temperature of the thermometer is at no time very widely removed from the ordinary. For such reasons, it has been possible, hitherto, to apply the boiling-point method only to the determination of the molecular weights of substances in solution. With the aid of the apparatus here described, we have already extended its application to the measurement of the electrolytic dissociation of solutions in ethyl alcohol, and work with this and other solvents is now in progress in this laboratory. As a measure of dissociation it will thus supplement the freezing-point method, which, as I have shown,[1] lends itself so well to water solutions.

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[1] Ber. d. chem. Ges., **26**, 797; Phys. Rev., **1**, 199.

[2] Ztschr. phys. Chem., **11**, 532.

[3] This JOURNAL, **17**, 507.

[4] Ztschr. phys. Chem., **12**, 624.

Although the boiling-point method possesses certain inherent points of weakness, yet a study of all the methods thus far proposed for carrying out such measurements, will show that in no single case has sufficient precaution been taken to remove all the possible sources of error, and, at the same time, to devise a form of apparatus simple enough to be well adapted to general practical use in the laboratory. This conclusion will be confirmed by an attempt to apply any form thus far suggested, to general use.

The following two points are to be urged against the methods now available, each being capable of producing serious error:

1. In no well-known form of apparatus thus far described has sufficient attention been given to the *effect of radiation of heat directly from the bulb of the thermometer outward upon the colder surrounding objects.* Where the apparatus is made entirely of glass, as is true of one of the best forms, judged by the results, proposed by Beckmann,[2] and also of his latest modification,[3] this point applies with special force, since neither the glass nor its liquid contents can cut off sufficiently the long heat-rays. Even when the inner tube is surrounded by a porcelain[4] or metallic jacket, containing the boiling solvent, there is no guarantee that the walls of this outer vessel are at the same temperature as the thermometer, since the two vessels are separated by a space through which the air can circulate freely. Much greater still is this source of error liable to be, when the inner vessel, in which the thermometer is placed, is simply surrounded by a jacket of asbestos, as in the apparatus of Orndorff and Cameron,[5] or that of

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[1] Ztschr. phys. Chem., **12**, 624; Phil. Mag., **36**, 465.

[2] *Ibid*, **8**, 224.

[3] *Ibid*, **21**, 246.

[4] *Ibid*, **15**, 663.

[5] This Journal, **17**, 517.

Sakurai;[1] the innermost layer of the asbestos receives heat from the boiling solution within, and also from the flame beneath, so that its temperature must be considerably higher than that of the thermometer itself.

That the effect of radiation cannot safely be disregarded can be shown experimentally by allowing the thermometer to come to the point of equilibrium in a boiling-point apparatus constructed entirely of glass, in a cool, dark room; then, keeping all other conditions constant and admitting the sunlight, a change will be noticed on the instrument. Where a method, even though it be a differential one, is thus dependent upon external conditions, it is clear that some precaution must be taken to eliminate this source of uncertainty. On the other hand, Raoult[2] has shown experimentally that the effect of radiation is negligible in the freezing-point method, which is just what one would expect, since here the difference in temperature between the thermometer and the surrounding metallic-bath containing the freezing-mixture, is at most only a few degrees.

2. An objection which applies to all the practicable forms, with that of Hite[3] and Sakurai[4] excepted, is, that *the condensed solvent is returned directly into the boiling liquid or solution in which the thermometer is immersed.* The thermometer can, therefore, never acquire the true temperature of equilibrium between the liquid and vapor phases, but must always come to rest at some point below this. This source of error has, however, been satisfactorily met in a form of apparatus constructed in this laboratory by Mr. Hite,[5] which is further removed from theoretical objections, and, for low-boiling solvents, has been shown by him to yield better results than any form thus far devised. It was, however, stated by the author that this apparatus "does not work with some heavy high-boiling liquids, probably on account of the great difference in temperature of the flask and surrounding air," his apparatus not being jacketed on the outside to prevent loss in heat by conduction.

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[1] J. Chem. Soc., **61**, 989.

[2] Revue Scientifique (Paris), 1894, **2**, 321.

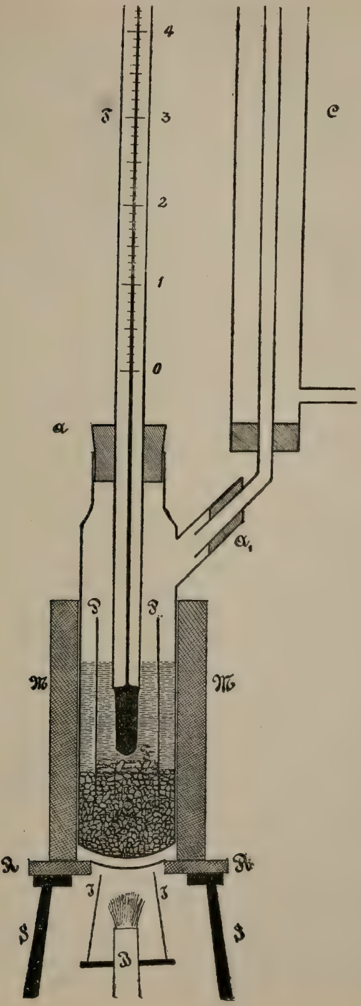
[3] This JOURNAL, **17**, 507.

[4] *Loc. cit.*

[5] *Loc. cit.*

Since this apparatus overcame so successfully, for the first time, the objection that the cold solvent is returned into the liquid in which the thermometer is placed, before it becomes heated again to the boiling-point, it seemed very desirable that it should be adapted to high- as well as to low-boiling solvents. It was with this object in mind that I began this work. The plan at first was to lengthen the Hite apparatus, jacket it on the outer side with a thick layer of asbestos to diminish the loss of heat by conduction into the cooler air, and then to jacket the outer side of the inner glass tube with a cylinder of thin platinum foil, which would be at very nearly the same temperature as the thermometer itself, and would therefore reduce the effect of radiation to a minimum. In the apparatus as first constructed, the inner glass tube was partly closed at the bottom, exactly as recommended by Hite, by means of a convex glass stopper, into whose edges notches had been filed to allow the passage of the vapor into the tube, which would establish the desired equilibrium in, and stir the liquid just around, the bulb of the thermometer. This was found to work very well with low-boiling solvents, but, like the form originally devised by Hite, it would not give satisfactory results with solvents whose boiling-points were above 100°. From some observations of my own it seems probable that this is due to the fact that the vapor under these conditions cannot enter the inner tube rapidly enough to prevent the liquid around the bulb from becoming superheated.

In the course of the work it occurred to me that it might be possible entirely to abandon the inner, glass tube in the Hite apparatus, using in its place simply the cylinder of platinum foil. This would both reduce the effect of radiation and prevent the condensed solvent from coming in contact with the thermometer until it was again reheated. It would, further, give better contact below between the liquid on the inner and on the outer side of the cylinder, than in the Hite form, and thus diminish the tendency of the solution on the inner side to become more concentrated than that on the outer. It would also allow the vapor to pass much more freely into the solution around the thermometer, and thus tend to prevent it from becoming superheated.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The Apparatus.

The form of apparatus which I finally devised and used, is shown in section in the figure, which is drawn approximately to scale. *A* is a glass tube 18 cm. high and 4 cm. in diameter. At the top it is drawn out to a diameter of about 2¾ cm. and ground to receive a ground-glass stopper. This tube is filled to a depth of from 3 to 4 cm. with glass beads. *P* is a cylinder of platinum 8 cm. high and 2½ cm. in width, made by rolling up a piece of platinum foil, and fastening it in position by wrapping it near the top and bottom with platinum wire. It would be still better if the edges of the cylinder were closed tightly by welding, so that none of the liquid could pass through from one side to the other. A cylinder of some other metal, such as copper, zinc, or silver could be employed in many cases, where they would not be acted upon by the solvent or the solution, but platinum is to be preferred because of its greater resisting-power to the action of such agents. Into the cylinder *P* some pieces of platinum foil are thrown. These are made by cutting foil into pieces about ¾ cm. square, bending the corners alternately up and down to prevent them from lying too closely upon one another, and serrating the edges with scissors to give a greater number of points from which the boiling can take place. The bulb of the thermometer is thus entirely surrounded by metal at very nearly its own temperature, except directly above. It was at first thought desirable to protect the bulb also from radiation upwards by forcing the thermometer through a hole cut in a circular sheet of platinum foil, which would then remain attached to the thermometer stem, and suspended just above the platinum cylinder *P*. But, in consideration of the comparatively small angle through which such radiation can take place, it was thought to be, under the conditions, a superfluous refinement. A condenser, *C*, about 40 cm. in length is attached to the tube A_1, which is 2 or 2¼ cm. in diameter, by means of a cork. When it is desired to protect the solvent from the moisture in the air, the top of the condenser-tube should be provided with a tube containing calcium chloride or phosphorus pentoxide. During an experiment the vessel, *A*, is closed above by a cork through which the Beckmann thermometer, *T*, passes. *M*, is a jacket of asbestos, 12 cm. high and 1½ cm. thick, over the top of which the rate of boiling can be observed very satisfactorily. It is constructed by bending a thin board of asbestos tightly around the tube *A*, and fixing it in place by means of copper wire. Thick asbestos paper is then wound around this until the desired thickness is reached. The apparatus is supported on a small iron tripod, *S*, 8 cm. in diameter, on which rests an asbestos ring, *R*, about 9 cm. in external diameter. A circular hole is cut in the center of this ring about 3½ cm. in diameter, and over this is placed a piece of fine, copper gauze. The source of heat is a Bunsen burner, *B*, surrounded by an ordinary metallic cone, *I*, to protect the small flame from the effect of air currents. The glass vessel, *A*, is shoved down until it comes in contact with the wire gauze. Under these conditions a very small flame suffices when low-boiling solvents are employed, and not a large flame is required when a solvent like aniline is used.

Carrying Out a Determination.

The glass beads are poured into the glass cylinder, the platinum cylinder inserted and pressed down into the beads to a distance of from ½ to 1 cm. The platinum plates are then introduced into the platinum cylinder, the end of the tube *A*, closed with a cork, and the ground-glass stopper inserted in *A*. The apparatus is then set in a small beaker-glass and weighed. The solvent is then introduced and the whole reweighed. Great care must be taken that not enough solvent is employed to boil over from one side of the platinum cylinder to the other. In case a laboratory is not provided with a balance capable of weighing accurately 200 or 300 grams, the solvent must be weighed directly and then poured into the apparatus. This, for low-boiling solvents, is necessarily less accurate than the above described method of procedure. After the solvent is weighed, the glass stopper is removed and the thermometer, fitted tightly into a cork, is placed in position, as shown in the drawing. The apparatus is then placed upon the stand in the mantle of asbestos, the cork removed from *A*, and the condenser attached. Heat is then applied and the solvent boiled. The size of the flame must be so regulated by means of a screw pinch-cock, that the boiling is quite vigorous, but not so violent as to be of an irregular or explosive character. A quiet but very active boiling is absolutely essential to the success of the experiment. The time required to establish the true temperature of equilibrium between the pure liquid solvent and its vapor is very much greater than in the case of a solution. This is strictly analogous to what is observed with the freezing-point method. Here the time necessary to establish the temperature of the equilibrium between the solid and liquid phases of the pure solvent is always much greater than for a solution. Before taking a reading on the Beckmann thermometer it is always necessary to give it a few sharp taps with a lead pencil, and indeed this should be done occasionally while the mercury is rising, and especially when it is near the point of equilibrium. The use of an electric hammer to accomplish this object is an unnecessary complication. A small hand-lens, magnifying a half dozen times, is quite sufficient to use in making the readings. It is always best to redetermine the boiling-point of the solvent. After this point has been settled, a tube containing the substance whose molecular weight it is desired to determine, pressed into pellets, is weighed, and a convenient number of these poured into the solvent, either through the condenser or directly through the tube *A*, when the solvent is not too volatile, and has ceased to boil. The tube is then reweighed, and the amount of substance introduced thus ascertained. The boiling-point of the solution is then determined.

The carrying out of a determination with a low-boiling solvent is a much easier process than with one boiling at a considerably higher temperature.

Thus, when anisol or aniline is employed, much care and some experience are necessary to determine the rate of boiling which must be adopted. If the boiling is too slow, the thermometer will never reach the temperature of equilibrium; if so rapid that it is irregular and explosive, the thermometer may rise above the true point and then suddenly drop below it at the moment when a large amount of the vapor is evolved. In a word, for high-boiling solvents, the rate of boiling must be as vigorous as possible, in order to proceed with perfect regularity.

All the forms of apparatus thus far devised are somewhat affected by the size of the flame used, provided, always, that the flame is large enough to produce rapid, and not large enough to produce explosive boiling. This is probably due to the corresponding change in rate at which the condensed solvent is returned to the boiling liquid. If this be the true explanation, then that form of apparatus which prevents the condensed solvent from coming in contact with the thermometer until it has been reheated, should be least affected by the size of flame used, and such is the fact. The apparatus of Hite, while not quite independent of the rate at which heat is added, is yet far less affected by a change in the size of the flame than any other form. The same point applies to the apparatus here described.

In all the determinations which I have made with my apparatus the barometer was carefully watched, but after the boiling-point of the solvent had been determined, the series of measurements could be carried out so quickly, that the changes in the barometer during this short interval were so slight that they could often be neglected. Whenever they were of appreciable value a correction was introduced into the results.

The Results.

The results which I have obtained are given in the subjoined tables. After the necessary details had been worked out, *every determination made was accorded an equal value, and every result is given.* No correction is introduced for the amount of the solvent which existed in the form of vapor or was condensed on the walls of the apparatus, since this could not accurately be determined. The solvents and the compounds whose molecular weights it was desired to determine, were purified by the methods best adapted to each case, and their degree of purity ascertained either by their melting- or boiling-point. The water was removed from the ether by sodium, from the benzene by fractional crystallization. The anisol and aniline were obtained sufficiently pure by fractional distillation. The anthracene was purified by boiling for two days with ethyl acetate, filtering, washing with cold ethyl acetate, crystallizing from glacial acetic acid, and subliming.

For several of the compounds used I am indebted to gentlemen working in this laboratory. For the acetanilid, to Mr. C. E. Waters; for the triphenylmethane to Mr. E. E. Reid; and for the diphenylamine to Mr. E. S. Smith.

To illustrate the speed of which the method is capable in its application, it may be stated that all the following determinations, including the adjustment of the thermometers for each solvent, were carried out in seven days.

The molecular weights are calculated from the well-known expression:

$$M = k\frac{d}{\Delta L}.$$

M is the molecular weight to be determined.
d, the amount of the substance used.
L, the amount of the solvent employed.
Δ, the rise in the boiling-point of the solvent.
k, a constant for each solvent.

SOLVENT, ETHER: $k = 2110$; boiling-point, 34°.9 at 760 mm.

Naphthalene, 128.

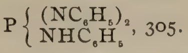
First Series.

	Ether. Grams.	Naphthalene. Grams.	Rise in boiling-point.	Molecular weight.
1	57.573	1.2365	0°.357	126.9
2	"	2.5155	0°.716	128.8
3	"	3.8733	1°.110	127.9
			Mean,	127.9

Second Series.

	Ether. Grams.	Naphthalene. Grams.	Rise in boiling-point.	Molecular weight.
1	53.830	0.8820	0°.273	126.7
2	"	1.8012	0°.558	126.5
3	"	2.9792	0°.920	126.9
			Mean,	126.7

SOLVENT, ALCOHOL: $k = 1150$; boiling-point 78°.3



$P\left\{\begin{matrix}(NC_6H_5)_2\\ NHC_6H_5\end{matrix}\right.$, 305.

	Alcohol. Grams.	Compound. Grams.	Rise in boiling-point.	Molecular weight.
1	57.805	0.8622	0°.056	306
2	“	1.3023	0°.087	298
			Mean,	302

SOLVENT, BENZENE: $k = 2670$; boiling-point 80.36 at 760 mm.

Naphthalene, 128.

First Series.

	Benzene. Grams.	Naphthalene. Grams.	Rise in boiling-point.	Molecular weight.
1	74.282	1.1178	0°.302	133.0
2	“	2.2798	0°.620	132.2
3	“	3.3608	0°.900	134.2
4	“	4.7243	1°.254	135.4
5	“	6.2973	1°.678	134.9
			Mean,	133.9

Second Series.

	Benzene. Grams.	Naphthalene. Grams.	Rise in boiling-point.	Molecular weight.
1	70.560	0.7594	0°.215	133.7
2	“	2.0548	0°.574	135.4
3	“	3.0780	0°.850	137.0
4	“	4.4790	1°.234	137.4
			Mean,	135.9

Third Series.

	Benzene. Grams.	Naphthalene. Grams.	Rise in boiling-point.	Molecular weight.
1	69.702	1.0240	0°.295	133.0
2	“	2.4527	0°.704	133.5
3	“	3.8387	1°.097	134.0
4	“	5.0807	1°.458	133.5
			Mean,	133.5

Fourth Series.

	Benzene. Grams.	Naphthalene. Grams.	Rise in boiling-point.	Molecular weight.
1	65.685	0.8175	0°.246	135.1
2	"	1.8895	0°.563	136.4
3	"	2.9787	0°.893	135.6
4	"	4.0707	1°.222	135.4
			Mean,	135.6

SOLVENT, ANISOL: $k = 4430$; boiling-point 152°.

Acetanilid, 135.

First Series.

	Anisol. Grams.	Acetanilid. Grams.	Rise in boiling-point.	Molecular weight.
1	59.210	0.6241	0°.270	173.0
2	"	1.2502	0°.538	173.9
3	"	2.2225	0°.946	175.8
4	"	2.8813	1°.220	176.7
			Mean,	174.8

Second Series.

	Anisol. Grams.	Acetanilid. Grams,	Rise in boiling-point.	Molecular weight.
1	59.872	0.6523	0°.282	171.1
2	"	1.5568	0°.676	170.4
3	"	2.1928	0°.926	175.2
4	"	3.0799	1°.270	179.4
			Mean,	174.0

Anthracene, 178.

First Series.

	Anisol. Grams.	Anthracene. Grams.	Rise in boiling-point.	Molecular weight.
1	60.298	0.7606	0°.276	202.5
2	"	1.4799	0°.530	205.1
3	"	1.8736	0°.685	201.0
			Mean,	202.9

Second Series.

	Anisol. Grams.	Anthracene. Grams.	Rise in boiling-point.	Molecular weight.
1	62.190	0.6053	0°.217	198.7
2	"	1.3279	0°.455	207.9
3	"	2.1170	0°.753	200.3
			Mean,	202.3

SOLVENT, ANILINE: $k = 3220$; boiling-point 182°.5 at 738 mm.

Triphenylmethane, 244.

First Series.

	Aniline. Grams.	Triphenyl-methane. Grams.	Rise in boiling-point.	Molecular weight.
1	60.126	0.8017	0°.180	238.6
2	"	1.6052	0°.353	243.5
3	"	2.2914	0°.496	247.4
4	"	2.9213	0°.654	239.2
			Mean,	242.2

Second Series.

	Aniline. Grams.	Triphenyl-methane. Grams.	Rise in boiling-point.	Molecular weight.
1	61.900	0.8956	0°.192	242.6
2	"	1.6312	0°.358	237.0
3	"	2.3258	0°.500	242.0
			Mean,	240.5

Diphenylamine, 169.

	Aniline. Grams.	Triphenyl-methane. Grams.	Rise in boiling-point.	Molecular weight.
1	64.220	0.7780	0°.224	174.1
2	"	1.3326	0°.391	170.9
3	"	1.7832	0°.535	167.1
			Mean,	170.7

Discussion of the Results.

Perhaps the fairest test of the efficiency of the several forms of apparatus which have been devised for carrying out the boiling-point method, is the relative accuracy of the results which have been obtained by their application.

The molecular weight of naphthalene in ether was worked out by Hite with his apparatus, in a series of seven determinations, using different concentrations of the solutions. His values vary from 128.9 to 130.8,[1] with a mean of 129.7.

The compound used with alcohol as a solvent was furnished by Dr. Gilpin, who desired that its molecular weight should be determined.

I regret that Mr. Hite did not bring under his investigation the determination of the molecular weight of naphthalene in benzene. Such determinations were, however, made by Orndorff and Cameron[2] in their apparatus. But since they have not taken the proper precautions either to reduce the effect of radiation to a minimum, or to prevent the cold solvent from coming in contact with their thermometer, their results are necessarily affected by uncertain and indeterminate errors. This is confirmed by a study of their results, which in many cases do not, for the same substance under the same conditions, agree at all satisfactorily with one another, and in a few instances such discrepancies amount to from 10 to 15 per cent.

Their determinations of the molecular weight of naphthalene in benzene agree, however, satisfactorily with one another, ranging from 141 to 145, with a mean of 143. Since my first series gave a value which was considerably lower, (133.9) I made a second, a third, and a fourth; in all, 17 measurements. The minimum value obtained was 132.2, the maximum 137.4, with a mean of the average values of the four series of 134.7.

As high-boiling solvents, anisol and aniline were chosen. Anisol is particularly interesting because it seems to effect a certain amount of polymerization of some substances when dissolved in it. Aniline, on the other hand, from the work of Beckmann,[3] does not, and is a good example of an easily obtainable high-boiling solvent, in which the experimental result should agree with the simplest, theoretical molecular weight.

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[1] A typographical error makes this value appear to be 138.8.

[2] *Loc. cit.*

[3] Ztschr. phys. Chem., 8, 226.

Orndorff and Cameron[1] have made three series of measurements of the molecular weight of acetanilid in anisol, with the following results :

I series, max. value 145, min. value 133, mean value 139.
II " " " 166, " " 147, " " 157.
III " " " 166, " " 148, " " 157.

It is difficult to see what conclusion can be drawn from such data, other than that there is probably a certain amount of polymerization of the anilide molecules, and even this conclusion depends upon which series of results is chosen. My own measurements in this case, be they right or wrong, have at least this merit, that they agree with one another as closely as could be expected. The results obtained by Orndorff and Cameron for anthracene in anisol are not more satisfactory than the last named. Here again they made three series of measurements:

I series, max. value 200, min. value 175, mean value 194.
II " " " 200, " " 168, " " 185.
III " " " 184, " " 176, " " 179.

The values which I have found for anthracene in anisol, ranging from 198.7 to 207.9, show, as they do with acetanilide, that there is, unmistakably, a considerable molecular condensation effected in the presence of this solvent.

The determinations in aniline as a solvent are directly comparable with those of Beckmann,[2] indeed, with the results of two modifications of his apparatus. The comparatively complex form described by him in 1891,[3] involving the glass jacket containing the same solvent, gave, as would be expected, better results than the simpler device described in 1896.[4] A series of determinations of the molecular weight of triphenylmethane in aniline, gave Beckmann values in his more complex apparatus, ranging from 246 to 252, mean 249 ; in his simpler, from 218 to 245, mean 233. The molecular weight of diphenylamine in aniline, as obtained by Beckmann in his more complex form, ranged from 169 to 170, in his simpler, from 164 to 173.

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[1] *Loc. cit.*

[2] Ztschr. phys. Chem., **8**, 226.

[3] *Ibid.*

[4] *Ibid*, **21**, 246.

The result of these comparisons shows that the simpler apparatus here described is capable of yielding as good results for low-boiling solvents as the form devised by Hite, and at least as satisfactory for high-boiling as the best form suggested by Beckmann, which is far more complex.

The objection of comparative complexity holds also with respect to the apparatus of Sakurai,[1] with which its inventor was able to obtain fairly satisfactory results. But since its application involves the subsequent analysis of each solution used, it can plainly never come into general laboratory practice, now that we have methods which are so much simpler and more direct.

The apparatus recently described by Beckmann,[2] to whom we are as much indebted for the experimental development of the boiling-point method as we are to Raoult for its theoretical, is much simpler than some of the forms which he proposed at an earlier date. The vapor jacket is abandoned for one of hot air, which is heated directly by the flame below, and is therefore not at the same temperature as the solution which it surrounds. The author naturally gives preference to the form in which the boiling liquid is surrounded by its own vapor at the boiling temperature.

Of the various forms of vapor jackets which have been devised, none of them seem to be entirely satisfactory. The first used was constructed of glass;[3] then this was abandoned in favor of metal, and this in turn by Beckmann for porcelain.[4] Recently objections have been raised by Fuchs[5] to the porcelain jacket. He has abandoned it, in turn, in favor of metal.[6]

When a metallic cylinder, such as I have described, is used by placing it within the boiling liquid itself, and metal is also placed beneath the bulb of the thermometer, at the same, or very nearly the same, temperature as the bulb, (which is the only safe method of preventing error from radiation), *the use of either a vapor or an air jacket is entirely superfluous.* Under these conditions, a thick roll of asbestos paper, which can be made in ten minutes and will last for months, answers every purpose.

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[1] *Loc. cit.* [2] *Loc. cit.* [3] *Loc. cit.*

[4] Ztschr. phys. Chem., **15**, 662. [5] *Ibid*, **22**, 72.

[6] It is impossible to judge of the relative merits of the apparatus described by Fuchs, since his paper is not accompanied by the experimental data necessary to test its value. But from its comparative complexity, it seems quite safe to predict that it will never find general application in the laboratory.

Conclusion.

The advantages claimed for the apparatus here described are:

1. It reduces the effect of radiation to a minimum.
2. It prevents the cold solvent from coming in contact with the thermometer until it has been reheated.
3. It renders entirely unnecessary the use of a vapor mantle on the outside of the boiling liquid, a simple jacket of asbestos, under these conditions, answering every purpose.
4. It is simpler, more easily constructed, and less difficult to manipulate, than any form thus far devised that is capable of giving results which are even fairly satisfactory.
5. It thus seems to meet the theoretical obligations of the method more nearly than any other form. That it meets the practical demands is shown by the results.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
April, 1897.

ALUMINUM ALCOHOLATES.

BY H. W. HILLYER.

In a former paper[1] we detailed the results of a research in regard to the action of aluminum on ethyl alcohol to which a small amount of fuming stannic chloride had been added. Since sending that paper to the publisher, other observations have been made, which add somewhat to our knowledge of this reaction; and similar studies have been made with methyl alcohol and the two propyl alcohols.

As stated in the article referred to, various anhydrous chlorides, which are soluble in alcohol, were used in an attempt to avoid a difficulty encountered in using mercuric chloride. When absolute alcohol is poured upon chipped aluminum and either platinic chloride, mercuric chloride, or stannic chloride is then added, a rapid deposition of the metal is soon noticed and then, with rise in temperature, an increasing evolution of hydrogen followed by a slower evolution, which is long continued, even on application of external heat. A large amount of aluminum is dissolved, enough, in some cases, to make the solution pasty or even solid with the product of the reaction. It has been found that sublimed ferric chloride will also, to a slight degree, bring about the action of aluminum on alcohol, and that even aluminum chloride produces a slight evolution of hydrogen when the chloride is freshly prepared by action of dry hydrochloric acid on metallic aluminum. External application of heat is necessary to the progress of any considerable reaction in the case of ferric chloride or aluminum chloride.

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[1] This JOURNAL, **19**, 37.

By passing dry hydrochloric acid gas into absolute alcohol standing over chipped aluminum, the metal is readily dissolved with evolution of hydrogen and development of heat. So much aluminum may dissolve in this way that on allowing the solution to cool it becomes solid by separation of a crystalline compound—probably an addition-product of alcohol and aluminum chloride. If, instead of passing into the alcohol a continuous stream of hydrochloric acid gas, a small amount of an alcoholic solution of the gas is added to the alcohol, the action is slower to begin, but increases in vigor till its rate is quite comparable with that induced by the use of anhydrous chlorides of the metals. This form of the reaction is very nicely shown by letting hydrochloric acid gas bubble into the alcohol standing over the chipped aluminum, but removing the gas delivery tube as soon as a fairly rapid evolution of hydrogen is noticed. The reaction will then continue at a good rate, if the mixture is slightly heated occasionally, for more than an hour, until enough aluminum has dissolved to make a jelly when mixed with an equal quantity of water. This hydroxide or basic chloride is, however, entirely soluble in a large quantity of water.

In all the cases noted, aluminum chloride has been added, or the conditions were such that it could be formed by decomposition of the hydrochloric acid or anhydrous chloride present. In the case of some of the alcohols, it was found when the stannic chloride was dissolved in a small portion of alcohol, and this solution then added to the main portion of the alcohol, that the action on the aluminum was more vigorous than when the same amount of the chloride was added to the whole of the alcohol. To explain this, it seems to us that in adding the stannic chloride to the smaller quantity of alcohol, the temperature was raised high enough to cause the formation of an addition-product of the alcohol and stannic chloride, and that it was upon this compound that the aluminum acted first, and that later it acted on an addition-product of the alcohol with the aluminum chloride which had been found. It is known that all of the anhydrous chlorides used form addition-products with common alcohol. Such addition-products are also known with other alcohols, and it may be said that we obtained a crystalline compound by action of stannic chloride on isopropyl alcohol—probably $SnCl_4$: $3C_3H_7OH$, as shown by analysis.

For a rapid and satisfactory solution of the aluminum, it may be desirable to have a "couple" of the more easily reducible metals and the aluminum, though our later experiments with hydrochloric acid gas seem to show that it isn ot necessary.

With the reactions involving the use of stannic chloride and hydrochloric acid gas, it is also necessary to have complete dehydration. When the reaction is in full career, the addition of a little water will nearly or entirely stop the action. In this respect there is another marked contrast with the reactions involving mercuric chloride where the presence of water seems to work no harm.

The observations made would then seem to show that, in general, it is necessary to a satisfactory action of aluminum on alcohol: that it should be anhydrous, that it should contain an anhydrous chloride with which it can form an addition-product, and that the aluminum should be coupled with a more easily reducible metal.

Aluminum Methylate.—The methyl alcohol used was dehydrated by anhydrous copper sulphate and subsequently distilled. Aluminum acts on methyl alcohol under conditions similar to those favorable to its action on common alcohol. On driving off the excess of alcohol a gelatinous mass remains, but on attempting to distil under diminished pressure, the mass does not fuse, but simply crumbles to a black powder and yields no condensable distillate. Only two reactions suggest themselves for the action of aluminum on methyl alcohol. They are expressed by the following equations :

$$2Al + 6CH_3OH = 2Al(OH)_3 + 3C_2H_6.$$
$$2Al + 6CH_3OH = 2Al(OCH)_3 + 3H_2.$$

It was found that the evolved gases, passed through sulphuric acid to retain the alcohol, when mixed with air, exploded violently and gave no indication of the presence of carbon dioxide when clear lime-water was added to the gaseous residue after the explosion, thus showing the presence of hydrogen only. From this the second equation seems the more probable during the first part of the reaction at least. At a later stage it might be that the nascent hydrogen acted on the methylate previously formed and changed it to the hydroxide, as indicated by the equation :

$$Al(OCH_3)_3 + 3H_2 = Al(OH)_3 + 3CH_4.$$

The following experiments show, however, that this is not the case.

In some cases, if not every case, the aluminum alcoholates are soluble in the alcohol from which they are derived. With this thought in mind, an attempt was made to determine whether aluminum methylate had really been formed, and decomposed on heating, or aluminum hydroxide had been the final product of the reaction of the aluminum on the alcohol. After a completion of a reaction with aluminum, methyl alcohol and stannic chloride, a large excess of methyl alcohol was added, and the whole allowed to stand over night. The liquid was decanted from an insoluble residue, and filtered out of contact with the air. In measured quantities of this solution, the aluminum and the chlorine were determined to ascertain how much of the aluminum could be accounted for as chloride. 10 cc. of the filtrate were diluted with water, acidified with hydrochloric acid, and the aluminum precipitated by ammonia. From this hydroxide 0.2245 gram of aluminum oxide were obtained, equivalent to 0.1189 gram of aluminum. To determine the chlorine, 10 cc. of the same solution were diluted with water, acidified with nitric acid, and brought to boiling. On adding silver nitrate a precipitate was formed, but it required persistent and very careful filtration to bring the filtrate to final clearness. The reason for this difficulty in clearing, and the cause of the failure of the silver chloride to become curdy has not yet been found. The silver chloride formed weighed 0.4113 gram, equivalent to 0.0897 gram of chlorine, an amount corresponding to 0.025 gram of aluminum as chloride.

Considering the similarity of the reaction with this alcohol to those of the other alcohols, and the fact of the evolution of hydrogen during the reaction rather than a hydrocarbon, the presence of aluminum in solution in a form not the chloride can be most easily explained on the supposition that the reaction is normal, that aluminum methylate is formed, but that it is decomposed on attempting to distil it.

Aluminum Propylate.—The normal propyl alcohol used in these experiments was dehydrated by anhydrous copper sulphate. It boils at 97°. In carrying out one of our experiments, 10 grams of aluminum and 150 cc. of alcohol were placed in a retort and then 2 cc. of fuming stannic chloride were slowly added. No perceptible effect was produced. On applying heat a slight evolution of gas occurred, but ceased on removing the source of heat. On adding 1 cc. of the chloride, an evolution of gas commenced, which was slow at first, but soon became so violent that external cooling was necessary to prevent boiling over. After this spontaneous action became weak, external heating induced further action, which continued several hours until the mass in the retort became quite viscous. In a subsequent experiment approximately the same amounts of aluminum and of alcohol were used, but instead of adding the chloride directly to the whole amount of the alcohol, it was first dissolved in a small quantity of the alcohol and then added. 5 cc. of stannic chloride were dissolved in 10 cc. propyl alcohol, and of this solution 2½ cc. were slowly added to the main bulk of the alcohol already standing on the chipped aluminum. Action did not become noticeable for about ten minutes, but then tin began to be deposited; a slow evolution of hydrogen was noticed, which rapidly increased, and soon became violent, as before.

The subsequent treatment of the product of reaction was similar to that used with the ethylate. The second of the two operations described above gave a much larger yield of the propylate on distilling, and it showed less indication of the presence of aluminum chloride by fumes at the commencement of the distillation. When the products were redistilled at a low pressure, they gave an amber-colored distillate, sometimes solidifying to a clear mass, which gradually became opaque, and sometimes immediately solidified to an opaque solid of the appearance and consistency of fresh commercial grape-sugar. By fractionating, a product was obtained melting at 65° and boiling under 15 mm. pressure between 235° and 255°. The first fractions were more yellow than the last fraction, which boiled with approximate constancy at 255°. The aluminum in the part boiling at 255° was determined by dissolving in nitric acid, heating the solution till oxidation was no more apparent, evaporating and igniting the residue. An amount of oxide, Al_2O_3, was left, which indicated 14.3 per cent. of aluminum. By dissolving in hydrochloric acid and precipitating with ammonia, the percentage of aluminum found was 13.2. There should be in aluminum propylate 13.1 per cent. of aluminum. The product, made by another operation and distilling between 257° and 262° at 20 mm. pressure, was analyzed by combustion. In order to protect it from the moisture of the air, it was melted and drawn into weighed glass bulbs with capillary ends, and these, after cleaning and weighing, were dropped into the combustion-tube. The combustion gave:

	Per cent.
H	10.4
C	53.4

The theory requires:

	Per cent.
H	10.2
C	52.9

Aluminum Isopropylate.—Isopropyl alcohol is acted on by aluminum in presence of stannic chloride with evolution of hydrogen under conditions like those used for the normal alcohol, but with less apparent readiness. On heating the product under diminised pressure, however, no distillation takes place, but a decomposition like that observed with methyl alcohol.

Amyl alcohol yields a volatile aluminum compound, of a yellow color, and boiling at 291° C. under a pressure of 12 mm.

By the use of aluminum as a reducing-agent, and stannic chloride, platinic chloride, or mercuric chloride as the sensitizing-agent, there seems no doubt that reduction may be performed in entire absence of water, when the substance to be reduced can be dissolved in any of the alcohols, in benzene, ether, or any solvent with which alcohol will mix when it is added to evolve hydrogen with the sensitized aluminum. From later experiments it is doubtful whether the presence of the precipitated tin, platinum or mercury, is essential. Commercial aluminum at least, containing slight impurities of carbon and iron, evolves hydrogen quite freely under the conditions indicated above, by starting the action with hydrochloric acid.

I wish to express here my hearty thanks to Mr. O. E. Crooker, and especially to Mr. R. F. Hastreiter, by whom much of the experimental work detailed above has been done in connection with graduating theses in this laboratory.

LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN,
MAY 1, 1897.

BEHAVIOR OF CHLORAL HYDRATE WITH AMMONIUM SULPHIDE.

BY JOSEPH LESINSKY AND CHARLES GUNDLICH.

While studying the reactions of chloral hydrate, we observed that when dissolved in water and mixed with a little ammonium sulphide, it threw down a precipitate only after a certain time had elapsed. This precipitate separated out almost instantaneously after a certain number of seconds had been counted. Upon further experiment we found that, if the concentrations are the same, the precipitate will appear, every time the experiment is tried, in exactly the same number of seconds, provided the temperature is the same.

At first we had considerable difficulty in repeating the experiment, as we had prepared a fresh quantity of ammonium sulphide. It was found, however, that this did not react with the chloral hydrate, even after standing a long time. We were more successful on using a well saturated solution of ammonium sulphide, and especially a solution that had been standing for several days, in other words, a solution of the polysulphides.

To show this reaction, the following conditions were observed:

Two grams of chloral hydrate were dissolved in 25 cc. of water, 10 cc. of this solution run out of a burette into a narrow beaker, and 5 cc. of yellow ammonium sulphide poured in, not run in. The liquids must be mixed as quickly as possible. It is best to shake the mixture slightly, and allow it to stand on a piece of white paper, so that the sudden appearance of the precipitate can be seen from a distance in showing the experiment.

At different temperatures the reaction is retarded or hastened, the time necessary for the precipitate to form being inversely proportional to the temperature and concentration.

At 1° C. the separation took place in 44 seconds.
" 20° C. " " " " " 19 "
" 45° C. " " " " " 8 "
" 65° C. " " " " " 3 "

For every 20° rise we have a gradual decrease in time.

The difference between 45° and 65° being 5 seconds.
" " " 45° " 20° " 10 "
" " " 20° " 1° " 20 "

The best way to show this reaction is to start a metronome ticking, mix the two solutions quickly and, while observing the mixture, count the number of seconds it takes before the precipitate appears. The exact nature of this reaction is not understood, especially as the resulting precipitate is evidently a mixture of sulphur and, perhaps, some sulphur compound of a mercaptan character, the odor being very characteristic. The precipitate was filtered off, and the solution, which was red, extracted with ether, the resulting oil emitting a very powerful odor and, when diluted with water, suggesting the odor of walnuts. If the concentrations of the two substances are changed, the resulting precipitate will vary in appearance. In our first experiments the precipitate was of a pinkish color, and the solution red; on heating a little on the water-bath, the precipitate became yellow and then brown, a remarkable succession of changes in color being observed. In the above mentioned experiments the precipitate was yellowish-brown in color, the solution itself being yellow, and on warming the precipitate, the color became almost black.

In order to obtain the pink precipitate, it is advisable to use an excess of chloral hydrate, but it requires some experimenting to obtain the conditions favorable for the formation of the precipitate.

Perhaps these reactions may be of value in the examination of chloral hydrate as to its purity. It is our intention to study the same, and also to determine the nature of the precipitate, and the cause of the "retarded precipitation."

There are only two such cases of retarded precipitation known to us, besides the one described by us, and, even in those cases, it has been impossible to ascertain the causes, although the reactions are not complicated, as in the case with the one described by us.

The reactions are as follows:

1. The action of sodium thiosulphate upon hydrochloric acid:

$$H_2S_2O_3 + \text{acid} = H_2O + SO_2 + S.$$

Here the sulphur separates out suddenly after a lapse of time.

2. The action of hydriodic acid with a starch solution when sulphuric acid is added:

$$2HI + H_2SO_4 + \text{starch solution} = 2H_2O + SO_2 + I_2, \text{ or}$$
$$2HIO_3 + 5SO_2 + 4H_2O = 5H_2SO_4 + I_2.$$

The last reaction is the most characteristic of the three, the iodine separating out so suddenly that most accurate results can be obtained in measuring the time. We have furthermore succeeded in procuring the same results by employing butyl chloral (croton chloral) instead of chloral hydrate, the resulting precipitate being of a beautiful lemon-yellow color. This last reaction is not as striking as the others, the precipitate requiring 2 or 3 seconds for complete separation.

New York College of Pharmacy,
New York, May 2, 1897.

A NEW AND RAPID METHOD FOR THE QUALITATIVE SEPARATION OF IRON, ALUMINIUM, CHROMIUM, MANGANESE, ZINC, NICKEL, AND COBALT.

By Alexander Ramsay Cushman.

Add ammonium chloride, ammonia to alkaline reaction, and then ammonium sulphide in slight excess. Warm and filter. Wash the precipitate and remove from the filter while still moist. Warm with moderately dilute hydrochloric acid in a porcelain dish. Complete solution of the precipitate shows the absence of nickel and cobalt. If a black residue remains, one or both are present, in which case add *aqua regia*, and warm gently until dissolved. Expel excess of acid and free chlorine by evaporation, and then make the solution strongly alkaline with ammonia, after previously adding ammonium chloride in case the amount of hydrochloric acid used upon the sulphides was small. Add bromine solution in excess, and allow to stand a few minutes. Filter and wash. The table given below shows the course of the analysis after this point is reached :

<table>
<tr>
<td>Precipitate 1.—Fe_2O_3, $MnO_2.H_2O$, $Al_2(OH)_6$, $Cr_2(OH)_6$. Remove from the filter and add KOH in excess, then Br solution and filter.</td>
<td colspan="3">Filtrate 1.—$ZnCl.2NH_4Cl$, $NiCl_2.NH_4Cl$, $[Cl.Co(NH_3)_5]Cl_2$. Add KOH in large excess, allow to stand a few minutes and filter.</td>
</tr>
<tr>
<td rowspan="2">Residue 2.—Fe_2O_3, $MnO_2.H_2O$. Divide in 2 parts.
<i>Part 1.</i> Dissolve in HCl, add a few drops of NH_4CNS. Blood-red color shows $Fe_2(CNS)_6$ and proves Fe.
<i>Part 2.</i> Fuse with $Na_2CO_3 + NaNO_3$ in O. F. of blow-pipe. Bluish-green mass proves Mn.</td>
<td rowspan="2">Filtrate 2.—$K_2Al_2O_4$, K_2CrO_4. Divide in 2 parts.
<i>Part 1.</i> Acidify with HCl, add excess of $(NH_4)_2CO_3$ and boil. A white flocculent precipitate shows $Al_2(OH)_6$ and proves Al.
<i>Part 2.</i> Acidify with $HC_2H_3O_2$ and add $Pb(C_2H_3O_2)_2$. A yellow precipitate shows $PbCrO_4$ and proves Cr.</td>
<td>Precipitate 3.—$Ni(OH)_2$. (Greenish-white). Confirm in salt of phosphorus bead in the R. F. of the blow-pipe. Yellow bead, cold, proves Ni.</td>
<td>Filtrate 3.—$[Cl.CO(NH_3)_5]Cl_2$, K_2O, ZnO. Heat to boiling and filter.</td>
</tr>
<tr>
<td>Precipitate 4.—$Co(OH)_3$ Confirm in borax bead, in the O. F. of the blow-pipe. Blue bead proves Co.</td>
<td>Filtrate 4.—Acidify with $HC_2H_3O_2$, and saturate with H_2S. A white, flocculent precipitate shows ZnS. Confirm by ignition with $Co(NO_3)_2$ on charcoal. Yellow-green mass proves Zn.</td>
</tr>
</table>

REVIEWS.

A RESUME OF PROGRESS IN THE CHEMISTRY OF THE CARBOHYDRATES DURING 1896.

Activity in this field has been unabated during the past year, and it becomes more and more evident to the student of the carbohydrates that these bodies present opportunities for the study and illustration of chemical theories in no way exceeded by their very great practical and technical importance. The following review is intended to include all of the publications appearing in the chemical journals during the year, although the practical impossibility of making the record complete is fully recognized. Purely technical papers have for obvious reasons not been included. The classification employed in former years has been retained.

General Reactions.—The continued study and development of new reactions among the carbohydrates has been so fruitful that these bodies may now be fairly regarded as among the most reactive of the general classes of carbon compounds. A large number of characteristic reactions have now been well studied, involving the general principles of polymerization, condensation, oxidation, reduction, ether, and ester formations, etc. Contrary to the former view that the carbohydrates were extremely unstable and sensitive compounds, it now appears that they are capable of undergoing the most manifold changes, not alone as regards their chemical features but in their physical properties as well. Indeed in this latter field it appears that the sugars offer the best known examples for the illustration of the principles of stereochemistry, while the latest researches indicate that sugar molecules are unstable systems in which a variety of intermolecular transformations may be induced. From their nature as derivatives of polyvalent alcohols containing several hydroxyls and, according to conditions, ketone, aldehyde, or carboxyl groups, it is of course to be expected that great facility for reaction would follow.

Tollens and his pupils[1] have produced a series of condensation-products between polyvalent alcohols and formaldehyde, called *formals.* The reaction occurs readily when equal parts of the alcohol, a 40 per cent. solution of formaldehyde and hydrochloric acid of 1.19 sp. gr. are heated together. The products are crystalline and stable with the probable constitution—as illustrated by trimethylenemannite—

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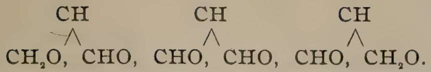
[1] Tollens, Henneberg, and Schulz: Ann. Chem. (Liebig), **289**, 20; **292**, 3; also Ztschr. Ver. Rübenzuck, Ind., 1896, 274.



$$\overset{\mathrm{CH}}{\overset{\wedge}{\mathrm{CH_2O,\ CHO}}},\ \overset{\mathrm{CH}}{\overset{\wedge}{\mathrm{CHO,\ CHO}}},\ \overset{\mathrm{CH}}{\overset{\wedge}{\mathrm{CHO,\ CH_2O}}}.$$

Sorbite also yields a triformal; adonite a diformal with one free hydroxyl; erythrite and pentaërythrite, diformals; glycerin a monoformal with a free hydroxyl, apparently in isomeric forms. Similar reaction follows with gluconic and saccharic acids.

A searching investigation upon the destructive action of more or less dilute mineral acids upon the monosaccharides, throws light upon several well-known reactions.[1] By heating dextrose, levulose, galactose, maltose, and arabinose with acids under different conditions of temperature, pressure, and time, and carefully estimating all of the decomposition-products, it was shown that the monosaccharides undergo three general phases of change which are largely independent of each other:

1. Condensation resulting in the formation of humus-like bodies.

2. Formation of levulinic and formic acids, resulting from a splitting off of a terminal carbon atom, accompanied by deoxidation of the system including the five remaining carbon atoms; a part of this oxygen goes to produce the formic acid or, under changed conditions, carbon dioxide. With the pentose sugars the result is similar. Humus-like bodies are more readily formed where the action occurs under pressure or in closed vessels. The characteristic reaction of the pentoses to yield furfurol occurs readily and, as is well known, almost quantitatively. It is interesting to note that both pentoses and furfural are endothermic compounds of almost identical degrees of heat-absorption, *viz.*, —86° and —88° calories respectively—which possibly explains the ready transition from one to the other.

3. The slow formation of carbon dioxide results in the case of the pentoses as well as in that of the hexoses.

The reaction between monovalent mercaptans and aldoses,[2] and between polyvalent mercaptans and aldehydes,[3] has now been extended to polyvalent mercaptans and aldoses.[4] The condensation occurs on heating the reacting substances in the presence of concentrated hydrochloric acid; the products are crystalline and more stable toward acids and more soluble than those with monomercaptans. Such compounds have been prepared between dextrose, galactose, mannose, xylose, and arabinose and ethylene, trimethylene, and benzoyl mercaptans.

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[1] Berthelot and André: Compt. rend., **123**, 567, 625.

[2] Fischer: Ber. d. chem. Ges., **27**, 674.

[3] Fasbender: *Ibid*, **20**, 460.

[4] W. T. Lawrence: *Ibid*, **29**, 547.

The aldose and ketose sugars form characteristic compounds with hydrazine hydrate[1] on digesting small amounts of the substances in methyl alcohol and crystallizing from ether. The constitution is supposed to be as follows:

$$CH_2OH.(CHOH)_4.CH{=}N{-}N{=}CH.(CHOH)_4.CH_2OH.$$

Such derivatives have been prepared from dextrose, fructose, and arabinose. Benzhydrazide also combines freely with aldose sugars in the presence of dilute alkalies.

Attempts have been made to utilize the properties of different hydrazines for the separation of sugars. Benzyl- and napthylhydrazine afford compounds of dextrose and fructose, which by their different solubilities permit such a separation. Methylphenylhydrazine is adapted to the isolation of galactose. Melibiose forms an insoluble compound with allylphenylhydrazine, which may be decomposed by benzaldehyde so as to free the sugar.[2] In a second paper the authors give in detail the results of their comparisons of the properties of methyl-, ethyl-, amyl-, benzyl-, and β-naphthylhydrazines of the various monosaccharides with the exception of fructose, sorbose, and mannose which form no insoluble compounds with the above.

A mixture of galactose and arabinose combines with benzhydrazide, but the arabinose derivative is insoluble and may be separated from the galactose compound. Both may then be decomposed by benzaldehyde, leaving the respective sugars free.[3]

An effort to determine the relation between configuration and lactone-formation seems not to have led to conclusive results.[4] *l*-Gluconic, *l*-gulonic, *l*-mannonic, *l*-arabonic, and α-glucoheptonic acids were studied in comparison with their stereoisomers: the gluconic and arabonic acids showed little tendency to lactone-formation but the dibasic acids were particularly active.

The theory of multirotation has received no important contribution as might have been expected to follow the announcement of Lobry de Bruyn and his associates in 1895 regarding the intramolecular transformations and changes in the optical properties of sugars under the influence of alkalies.[5] The priority of the suggestion of this cause of multirotation is claimed by von Lippmann, as recorded in his work *Chemie der Zuckerarten*, p. 130.

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[1] E. Davidis: *Ibid*, **29**, 2308.

[2] W. van Ekenstein and C. A. Lobry de Bruyn: Recueil trav. chim., **15**, 97, 225.

[3] E. Subasshow: Ztschr. Ver. Rübenzuck-Ind., 1896, 270.

[4] E. Hjelt: Ber. d. chem. Ges., **29**, 1867.

[5] *Ibid*, **20**, 3078.

It is pointed out that the supposed destruction and loss of sugar in factory-processes through the use of lead oxide or hydroxide is really due to a change in the rotary form of the sugar through the influence of the alkali.[1]

The decomposition of sugars heated with alkalies, and the appearance of brown color in such solutions is proportional to the temperature and concentration of alkali. If air is excluded no brown color results under a temperature of 45° nor is lactic acid produced, but if the solutions are boiled with free access of air the decomposition goes on more rapidly and lactic and formic acid result.[2]

New Synthetic Sugars.

Fischer has added two more to his long list of synthetic sugars by employing his already familiar methods. From xylose was obtained xylonic acid;[3] this, by heating with pyridine becomes transformed into the new stereoisomeric lyxonic acid which by reduction with sodium amalgam yielded lyxose, a new sugar belonging to the dulcite series. The author predicts its preparation by Wohl's "Abbau" method from galactose. In a similar way rhamnose was transformed through the stages of rhamnonic acid and isorhamnonic acid to isorhamnose, a methylpentose stereoisomeric with rhamnose.[4]

Monosaccharides.

Pentoses.—The qualitative reaction of the pentoses and pentosans with phloroglucin has been carefully studied.[5] On warming these substances with concentrated hydrochloric acid and phloroglucin a red color is produced which, with transmitted light, gives characteristic spectrum absorption-bands. The color separates as a sediment which may be filtered out and redissolved in alcohol, rendering the reaction much more sensitive. Other sugars give a colored solution, but no absorption-bands.

The separation of arabinose from galactose by means of the benzhydrazide reaction has already been referred to under "general reactions." Arabinose forms a compound with bromal similar to those with chloral.[6]

Rhamnose seems to be to some extent assimilable in the digestive tract, experiments showing that by healthy persons eight per cent., and by a diabetic patient sixteen per cent. of the amount administered, was excreted unchanged.[1]

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[1] C. Lobry de Bruyn and W. van Ekenstein: Recueil trav. chim., **15**, 92.

[2] F. Framm: Pflügers Archiv., **64**, 575.

[3] E. Fischer and O. Bromberg: Ber. d. chem. Ges., **29**, 581.

[4] E. Fischer and H. Herborn: *Ibid*, **29**, 1961.

[5] B. Tollens: *Ibid*, **29**, 1202.

[6] Hanriot: Compt. Rend., **122**, 1127.

By fractional crystallization different modifications of rhamnose (isodulcite) have been noted; *e. g.*, β-isodulcite $[(\alpha_D = 10^\circ$ to $12^\circ]$ and γ-isodulcite $[(\alpha)_D = 20^\circ]$.[2]

With reference to the formation of furfurol from pentoses and pentosans, Tollens has repeated former experiments with glucuronic acid and its derivatives.[3] By distilling the acid with hydrochloric acid of 1.06 sp. gr., from 15 to 17 per cent. of furfurol was obtained, or something less than the theoretical amount. The derivatives of the acid also yielded furfurol in large quantities.

Hexoses.—Dextrose compounds with polyvalent mercaptans, with hydrazine hydrate and alkyl hydrazines, have been referred to under "general reactions." Galactose has been prepared from a kind of gum occurring in wine.[4] Galactosamine[5] loses one-half of its ammonia when boiled with methyl alcohol, and the residue has the same composition as the "osamine" of mannose.[6] A compound between galactose and choral has been obtained which still retains the power to reduce Fehling solution, and gives a red color with orcin chloride.[7]

Molecular modifications of galactose with varying rotatory power are reported as resulting from fractional precipitation of the sugar by absolute alcohol in the presence of dilute alkalies; *e. g.*, β-galactose $[(\alpha)_D = 81^\circ.6]$ and γ-galactose $[(\alpha)_D = 53^\circ)$. In watery solutions these forms revert to the normal galactose.[8] A crystalline substance has been extracted from the seed of the yellow lupine, which by hydrolysis yielded galactose, but it does not appear that it was a hexavalent alcohol, although named galactite.[9] Compounds of galactose with chloral and polyvalent mercaptans have been referred to elsewhere.

Mannose has been obtained in crystalline form from a solution in absolute methyl alcohol and ether. It melts at 132°, and exhibits multirotation from $(\alpha)_D = -13^\circ.6$ to $+14.^\circ 25$.[10]

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[1] L. Lindemann and R. May: Deutsch. Archiv. f. klin. Med., **56**, 283.

[2] Tanret; Compt. Rend., **122**, 86.

[3] B. Tollens and F. Mann: Ann. Chem. (Liebig), **290**, 155.

[4] G. Niviere and A. Hubert: Rev. inter. falsific., **9**, 48.

[5] Ber. d. chem. Ges., **28**, 3082.

[6] C. Lobrey de Bruyn and F. van Leent: Recueil. trav. chim., **15**, 80.

[7] Hanriot: Compt. Rend., **122**, 1127.

[8] C. Tanret: Bull. Soc. Chim. (Paris), [3], **15**, 5.

[9] H. Ritthausen: Ber. d. chem. Ges., **29**, 896.

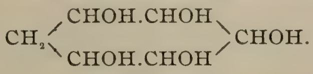
[10] W. van Ekenstein: Recueil. trav. chim., **15**, 221

The two stereoisomeric methyl-mannosides,[1] on being mixed in molecular proportions, give an optically inactive mixture. On crystallizing at a temperature of 8° or lower, the two isomers crystallized separately, and by allowing the crystallization to proceed *in vacuo*, crystals of unusual size were obtained, which could be mechanically separated. Crystallization above 15° yielded only the racemic compound. This would indicate that the racemic formation occurs under heat-absorption.[2]

The occurrence of sorbose in fermented fruit juices is now accounted for by the isolation of a microbe which exerts an oxidizing influence on sorbite. Inoculation of this microbe into solutions containing sorbite, suffices to produce sorbose.[3]

Volemite, the heptavalent alcohol identified in 1895,[4] while evidently of carbohydrate nature, does not undergo hydrolysis with sulphuric acid, is non-fermentable, and does not react with phenyl hydrazine, although it combines with acetyl chloride, acetic aldehyde and benzaldehyde.[5]

The true position of quercite as a carbohydrate is still doubtful.[6] By oxidation with nitric acid it yields mucic and trihydroxyglutaric acids; with permanganate, malonic acid. The latter indicates the correctness of Kannonikow's formula,



$$\mathrm{CH_2}\left\langle\begin{matrix}\mathrm{CHOH.CHOH}\\ \mathrm{CHOH.CHOH}\end{matrix}\right\rangle\mathrm{CHOH.}$$

Disaccharides.

Sucrose.—A very thorough study has been made by J. H. Long of the action of salts upon solutions of sucrose. The results of the investigation show that sucrose solutions are completely inverted by a large number of different salts. The action is slow at ordinary temperature, but increases rapidly above 60°; the action is also influenced by light. Apparently the inversion follows the general law governing the action of weak acids on sugars. Although all conditions of concentration, temperature, etc., were carefully controlled, the inversion coefficient was not constant for different salts.[7] Solutions of pure sucrose of 10 and 50 per cent. strength acted upon by sulphurous acid at temperatures from 30° to 80°, showed that inversion resulted in this case as well as with other acids in accordance with the Guldberg–Waage law. The same was found true in the presence of salts and other impurities.[1]

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[1] Ber. d. chem. Ges., **28**, 1145, 1167.

[2] E. Fischer and L. Beensch: Ber. d. chem. Ges., **29**, 2927.

[3] G. Bertrand: Compt. Rend., **122**, 900. [4] Ber. d. chem. Ges., **28**, 1973.

[5] E. Bourquelot: J. Pharm. Chim. [26], **2**, 385.

[6] H. Kiliani and J. Schäfer: Ber. d. chem. Ges., **29**, 1762.

[7] J. H. Long: J. Am. Chem. Soc., **18**, 121, 693.

The electrical resistance of a solution of sucrose is a function of its concentration, the minimum being with a solution of a gram-molecule in something more than 10 liters of water. With a constant current the resistance is a function of the temperature, diminishing as $t°$ increases. The current seems to produce only an inappreciable transport of sugar to the positive pole.[2]

A report on the use of Schollmeyer and Huber's electrolytic method for the purification of sugar solutions in factory operations, shows that the result is satisfactory, but that electrolysis alone cannot successfully compete with the lime process of clarification. The success of the present process is due to its combination with the lime process.[3]

The effect of basic lead acetate upon sugar solutions has been carefully studied, and a number of important conclusions drawn, mostly of technical application: among these, that the presence of basic lead acetate affects the rotation of sugar solutions, through the formation of lead compounds. In the presence of baryta, strontia or lime, lead saccharates are precipitated; magnesia is also efficient in this respect. Raffinose[4] is thrown down from aqueous solutions by very basic lead acetate.

In an address on the origin of sugar in the beet, F. Strohmer reviews in an interesting manner the physiology of the sugar-beet. The total amount of water and sugar present during the latter half of the growth of the beet is practically constant; the sugar is prepared in the leaf and its amount depends on the vigor and extent of this part of the plant. When removed from the earth the beet steadily loses sugar by the process of transpiration.[5] Sucrose is said to be formed from the starch in potatoes by freezing (see Starch).

A new method for recovering sucrose from beet-molasses has been patented by G. Kassner.[6] After treatment with lime or basic acetate of lead the filtered solution is slightly warmed, and treated with a thin paste of lead oxide or hydroxide, which precipitates the sucrose as a lead compound. One molecule of sugar requires somewhat more than two molecules of lead oxide, PbO. The lead saccharate is sufficiently insoluble to permit of washing, and is afterwards decomposed by carbon dioxide. The lead carbonate is recovered by ignition. Criticisms of this process, both pro and con, have been published.[1] It does not appear that with proper manipulation there is danger of any lead compounds remaining in the crystallized sugar.

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[1] K. Stiepel: Ztschr. Ver. Rübenzuck-Ind., 1896, 654, 746.

[2] F. von Siegroth: Elektro. Chem. Zeit., **3**, 33.

[3] Baudry: *Ibid*, July 5, 1896.

[4] H. Suoboda: Ztschr. Ver. Rübenzuck-Ind., 1896, 107.

[5] F. Strohmer: Oesterr-Ung. Ztschr. Zucker-Ind. u. Landw., **25**, 589.

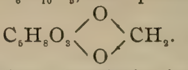
[6] G. Kassner: *Ibid*, **25**, 800.

Another patent relating to the same process involves treatment of the molasses with alkali or calcium sulphite and sulphur dioxide, and heating to boiling under pressure.[2]

Amorphous Carbohydrates.

Cellulose.—The valuable researches of Cross and Bevan and their associates upon the constitution of the celluloses is still progressing and with notable results. Reports from these authors during the past year have reference mainly to the cellulose of cereal straws. By dissolving bleached straw-cellulose in concentrated sulphuric acid, and then diluting with water, a precipitate was obtained which was practically free from substances yielding furfurol; the soluble portion retained practically all of such materials originally present in the straw. On neutralizing this solution with barium carbonate a portion of these materials was thrown down, but the solution still reduced Fehling's solution strongly; the osazone derived from it melted at 154°; analysis indicated a substance with C_{16} to C_{18}; by oxidation, acetic acid was produced, and there was evidence of the presence of hydroxyl groups capable of acetylization. The cereal straws are made up of the following constituents: Ligno-celluloses, 33 per cent.; resistant celluloses, 25 per cent.; hemicelluloses, 21 per cent.; pentosans, 21 per cent.[3]

An attempt to trace the development of the various celluloses and related substances in the growing plant (barley) has given interesting results.[4] Substances yielding furfurol were found in both the soluble and the permanent tissue, but these are localized in the cell-substances, and are generally changed into permanent tissue. In the growing plant the "furfuroids" are separated from the cellulose by 1 per cent. sulphuric acid at a pressure of three atmospheres. In the early stages of growth the "osazones" melt at 180°–190°, *i. e.*, are not pentose compounds. Up to the flowering period the products of hydrolysis are fermentable, and do not yield carbon dioxide when oxidized with hydrogen peroxide. From the flowering period on there is no constant increase of the pentosan-formal complex.

From the mature straw the portion separable by sulphuric acid has the empirical formula $C_6H_{10}O_5$, and probably the constitution of a pentosan-formal,  $C_5H_8O_3\left\langle\begin{matrix}O\\O\end{matrix}\right\rangle CH_2$. It yields the "osazones" of the pentoses after hydrolysis, is characteristically decomposed with formation of carbon dioxide, and the product of hydrolysis is partially fermentable. The authors regard the furfurol-yielding substances as direct products of assimilation.

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[1] See A. Wohl: Ztschr. Ver. Rübenzuck-Ind., 1896, 159; "C. W.," Dingler's Pol. J., **301**, 46; G. Kassner: *Ibid*, **301**, 215; Pharm. Cent. H., **37**, 4.

[2] K. Kastengren, Boehm: Ztschr. f. Zuck-Ind., **20**, 279.

[3] Cross, Bevan and Beadle: J. Am. Chem. Soc., **18**, 16.

[4] *Ibid*, p. 8; Cross and C. Smith: Chem. News, **74**, 175: Ber. d. chem. Ges., **29**, 1457.

Former experiments upon the rise in temperature of cellulose through the absorption of atmospheric moisture,[1] have been continued, the results indicating that "viscoid," a form of cellulose precipitated from solutions in alkali and carbon disulphide, behaves in this respect like finely divided cotton.[2]

Experiments upon the saccharification of sulphite-cellulose and sawdust, for the purpose of producing alcohol[3] by the fermentation of the product, showed that 0.4 to 0.6 per cent. sulphuric acid acting at eight atmospheres pressure during two hours produce 45 per cent. of sugar from sulphite-cellulose. 0.5 per cent. sulphuric acid at nine atmospheres pressure during one-fourth hour produced 22.5 per cent. sugar from sawdust. From 100 parts of sawdust, 6.5 parts of pure alcohol were obtained. A tetranitrocellulose of marked explosive properties has been prepared by the action of nitric acid on dinitrocellulose in the presence of strong dehydrating substances like sulphuric acid and phosphorus pentoxide.[4]

Certain cellulose derivatives give promise of such industrial value as to warrant the securing of patents by their originators. Cross and Bevan have patented in England and Germany a process for preparing cellulose tetracetate by heating dehydrated cellulose and zinc acetate with acetyl chloride. The product is solid, but dissolves in chloroform and resembles collodion without possessing its explosive character.

Chardonnet and Lehner have patented in Germany a method of making an imitation of silk ("Glanz-cellulose"). A description[5] states that the glistening appearance is due to the fact that the fibres are solid. It is produced by nitrating cellulose, dissolving in alcohol and ether, passing the viscous mass through fine holes, and allowing the solvent to evaporate; the fine threads are spun to yarn, and denitrated by ammonium sulphide, after which it is no longer explosive or combustible. The silk is more hygroscopic than ordinary cellulose, and less elastic, and only 70 per cent. as strong as silk.

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[1] Chem. News, **71**, 1.

[2] C. Beadle and O. Dahl: Chem. News, **73**, 180.

[3] E. Simonson: Norsk. tekniks. Tidskrift, 1895, 65.

[4] H. N. Warren: Chem. News, **74**, 239.

[5] Cross and Bevan: J. Soc. Chem. Ind., **15**, 317.

An oil and water-proof paper has been patented by E. Schering. It is prepared by saturating hydrocellulose (parchment paper) with pyroxylin.

The hemicellulose of the thickened cotyledons of seeds of lupine previously shown to yield galactose and a pentose on hydrolysis, has been studied during the process of germination and is found to be largely absorbed. It undoubtedly serves as a reserve material in the seed.[1]

Analysis of xylan carefully prepared from corn-cobs and dried by a special method, shows its composition to be represented by the formula $C_5H_8O_4$. A similar preparation from birchwood gave the formula $C_4H_6O_3$. It is suggested that this is a tetrosan and further study is reserved. Mannan from vegetable ivory has a composition represented by $C_6H_{10}O_5$.[2]

Starch.—A study of the progressive hydrolysis of starch by acids, controlled by frequent determination of rotation and reducing-power, shows a constant relation between these two properties at all stages of hydrolysis.[3] The conclusion is drawn that in any acid-converted starch-product the specific rotation represents a definite composition, and in such a product but three simple carbohydrates exist. The speed of hydrolysis follows about the same law as sucrose.

The starch of potatoes which have been frozen or kept for some time at a temperature near the freezing-point, is changed to sugar (sucrose and dextrose). If such potatoes are returned to ordinary temperature, in time some of the sugar disappears in the process of transpiration, and a large portion (about 62 per cent.) is changed back to starch.[4]

Starch paste is changed by chloroform into modifications similar to those produced by the action of acids. A solution of starch in contact with chloroform for three months no longer gave the usual reaction with iodine. By evaporating the solution and precipitating with alcohol, dextrins of varying solubility were obtained.[5]

Iodine and starch form a chemical compound, *e. g.*, starch is able to withdraw iodine from other compounds, forming iodide of starch. From the latter compound the iodine is separated by dialysis in the form of hydriodic acid.[6]

Starch exposed to a solution of chloral swells up to a nearly clear, viscous solution. After filtration such a solution gives no color reaction with solid iodine : if water be added to this solution, a blue color appears at the zone of contact with the iodine. These and other reactions show a restrictive influence of chloral on the formation of the starch-iodine compound.[1]

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[1] E. Schulze: Ztschr. phys. Chem., **21**, 392.

[2] S. W. Johnson: J. Am. Chem. Soc., **18**, 214.

[3] G. Rolfe and G. Defren: *Ibid*, **18**, 869.

[4] W. Bersch: Oesterr-Ung. Ztschr. Zuck-Ind. u. Landw., **25**, 766.

[5] F. Musset: Pharm. Centr. H., **37**, 587.

[6] *Ibid*, **37**, 556.

The isomaltose of Lintner and Düll, and others, is still regarded as of doubtful existence. Among the products of diastatic action upon starch, isomaltose is said to be formed. It is pointed out that different dextrins result, of which the so-called No. III resembles maltose, but is not easily fermented by yeast of the Saaz or Frohberg types, these properties being characteristic of isomaltose. If, however, the experiments be made *in vacuo*, this product is readily fermentable. This is explained on the principles of osmosis, fermentability being dependent upon the diffusibility of the substance through the cell-membrane. Moreover, this dextrin III, if mixed with about 20 per cent. of maltose, gives an "osazon" like that described for isomaltose. The author regards isomaltose as a mixture of maltose and certain dextrins.[2]

Isomaltose may be prepared by the action of sulphuric acid on dextrose at ordinary temperature for some months. By precipitation with alcohol and ether, about 27 per cent. of the original sugar was obtained as a product of a specific rotation of $+70°$ and a reducing-power two-thirds that of dextrose. In a similar way maltose may be condensed to isomaltose.[3]

Methods of Analysis.

A careful review of all of the methods for the quantitative estimation of the pentoses and pentosans leads to the conclusion that the gravimetric precipitations of furfurol obtained by distillation of the material with hydrochloric acid of 1.06 sp. gr. with either phenyl hydrazine or phloroglucin is the most satisfactory ; on some accounts the latter reagent is preferred. The weight of phenyl hydrazine precipitate $\times$ 0.9676 $=$ weight of pentosan in original material. The weight of phloroglucin precipitate divided by the factor 1.82 to 1.93 $=$ furfurol, which multiplied by 1.84 $=$ weight of pentosan in original material.[4]

A rapid and accurate method of determining the amount of copper thrown down by reducing sugars is to filter on a porcelain Gooch crucible, and ignite until the cuprous is changed to cupric oxide. Tables are given for the values of dextrose, lactose, and maltose in terms of cupric oxide.[1]

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[1] E. Schar : Pharm. Centr. H., **37**, 540.

[2] E. Prior: Centr. Bl. f. Bakt. u. Parasiten-kund., **2**, 271 ; also Forsch: Ber. ub. Lebensm. u. Bez. Z. Hyg., **3**, 322.

[3] H. Ost: Chem. Ztg., **20**, 761.

[4] B. Tollens, F. Mann, M. Kruger : Ztschr. angew. Chem., 1896, 33 ; also J. f. Landw., 1896, 171.

By adding potassium cyanide to Fehling's solution until the blue color disappears and then a measured excess of Fehling's solution, the mixture may be titrated with reducing sugars to the point where the blue color disappears and the amount of sugar calculated. This is said to be less accurate and convenient than a similar method previously suggested, involving the use of potassium ferrocyanide.[2]

By boiling a measured amount of sugar solution with an excess of Fehling's solution, the excess of the latter may be determined by adding phenyl hydrazine choride and measuring the nitrogen gas thus liberated.[3]

The removal of lead from sugar solutions clarified by means of basic lead acetate, may be accomplished by the use of ammonium oxalate. The ammonia thus freed is without effect on the determination.[4]

Ammoniacal silver nitrate is quantitatively reduced by solutions of glucose, levulose, and galactose; sucrose, starch, and dextrin are without effect, while lactose and maltose reduce irregularly, owing to continued hydrolysis by the ammonia.[5]

Since the specific rotation of levulose changes at different temperatures, this property may be turned to account for its estimation in the presence of dextrose. The rotation of a mixture of dextrose and levulose diminishes regularly from 0° to 88° at which it becomes zero. By observing the total variation, data are obtained for a formula to be employed in calculating the results of analytical observations. A special observation tube is necessary for the polarimetric readings at low temperature. It is also noted that at 0° the rotation does not become constant for some hours.[6]

Lactose may be estimated in milk by precipitating the caseïn with phenol and basic lead acetate. From the filtrate lead may be removed by sodium sulphate.[7]

If milk is clarified by boiling with basic lead acetate, sugar is destroyed. The results of polarimetric determination are usually lower than by gravimetric methods.[8]

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[1] G. Defren: J. Am. Chem. Soc., **18**, 749.

[2] A. Gerrard: Pharmzeut. J., 1895; Causse: J. pharm. Chim. (6), **3**, 433.

[3] E. Riegler: Wien. Med. Blätter, 1896, 451.

[4] Zamaron: Bull. Ass. Chim., 1895, 346.

[5] J. Henderson: Chem. News, **73**, 81.

[6] H. W. Wiley: J. Am. Chem. Soc., **18**, 81; see also Allen's Commercial Organic Analysis, Vol. I, p. 291.

[7] B. van Ketsl, Nederl, Tijdschi: Pharm., **8**, 151.

[8] E. V. Raumer and E. Spath: Ztschr. anorg. Chem., 1896, 70.

In correction of a method formerly proposed for the estimation of lactose,[1] double the normal weight of milk is taken, clarified with mercuric nitrate, diluted to 100 cc., and polarized in a 400 mm. tube. The same process is repeated with a sample diluted to 200 cc. The data thus obtained are used in calculating the true volume of liquid and the precipitate in the flask. The true polarization is found by dividing the product of the two readings by their difference.[2]

Papers on the methods of examination of honeys have appeared which, however, are too long and too technical for intelligent abstraction in this place.[3]

Acetylene gas has been found an unusually desirable illuminant for the polarimeter, giving a distinct field of view where other sources of light utterly failed.[4]

A comparison of the different methods of determining cellulose or "crude fibre" leads to the conclusion that none of the methods thus far proposed satisfies the requirements of accuracy and rapidity. With most methods the "crude fibre" still retains pentosans or oxycellulose. Others which overcome this difficulty attack the cellulose itself.[5]

Action of Ferments.

The action of animal secretions on the polysaccharides has been studied under a wide range of conditions and with many different materials, including blood serum and infusions from various glands and organs of different warm- and cold-blooded animals. In all cases starch, glycogen, and maltose were changed to dextrose. Lactose was not changed by blood serum nor was sucrose. In general, the latter was but little affected. Trehalose was slightly changed in some cases, in others not. Raffinose was unchanged by either blood serum or intestinal juices; α-methyl-glucoside was unchanged but methyl-glucoside was decomposed by an infusion of the intestinal membranes of the horse. Amygdalin was unchanged by the intestinal infusion of ruminants but speedily decomposed by that of other mammals.[6]

Experiments indicate that a sugar not fermentable by a certain organism is still unfermentable when mixed with a second fermentable sugar.[7]

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[1] J. Am. Chem. Soc., **6**, 289.

[2] H. W. Wiley and E. Ewell: *Ibid*, **18**, 428.

[3] E. Beckmann: Ztschr. anal. Chem., **35**, 263; also O. Kunnemann and Hilger: Forsch. Ber. u. Lebensm., etc., **3**, 211.

[4] H. W. Wiley: J. Am. Chem. Soc., **18**, 179.

[5] H. Suringar and B. Tollens: Jour. f. Landw., 1896, 343.

[6] E. Fischer, Sitzungs: Ber., Kgl. Preuss. Akad. d. Wiss., Jan., 1896; also E. Bourquelot and E. Gley: Compt. Rend. Soc. Biol., 1895, 555.

[7] Van Laer: Bull. Assoc. belge. Chimistes, **9**, 319.

By extracting cultures of *aspergillus niger* with water, a soluble ferment is obtained which produces very complete hydrolysis of raffinose, the rotation diminishing from 103° to 50°. An infusion of baker's yeast gave similar results.[1]

Brown and Morris have called attention to an enzyme (cystase) which dissolves cellulose but is rendered inactive at 60°.

Other enzymes are thought to exist which are able to hydrolyze the hemicelluloses, such as arabo-xylan, galacto-araban, etc., but at temperatures below 60°.[2]

A saturated solution of gypsum seems to retard diastatic action temporarily, but, later, saccharification is increased.[3]

W. E. STONE.

PURDUE UNIVERSITY, Feb. 27, 1897.

TRAITÉ ÉLÉMENTAIRE DE MÈCANIQUE CHIMIQUE FONDEE SUR LA THERMODYNAMIQUE. Par P. Duhem, professeur de physique théorique a la faculté des sciences de Bordeaux. Tome I, Principes Fundamentaux de la Thermodynamique, Faux Équilibres et Explosions. Librairie Scientifique, A. Hermann. Paris, 1897. pp. 299.

In order that the contents of this work may be more readily comprehended, the author has prefixed a chapter on the fundamental mathematical conceptions underlying analysis and mechanics. This volume is divided into two books. The first, treating of the *Fundamental Principles of Thermodynamics*, including in part, the doctrine of the conservation of energy, thermochemistry, entropy and thermodynamic potential, the general equations of thermodynamics, perfect gases, stability and isothermic displacement of equilibrium, stability and isentropic displacement of equilibrium, displacement of equilibrium by variation of temperature.

The second has to do with the so-called cases of *False Equilibrium* and with *Explosions*, discussing in four chapters, viscosity and friction, false chemical equilibrium and the point of reaction, the velocity of reactions, and explosions.

As M. Duhem states, this is not an experimental treatise, but chiefly a theoretical and mathematical one. It is, therefore, not a work on physical chemistry as such, in the sense of the *Lehrbuch* of Ostwald, since physical chemistry is, and probably will remain for a long time, primarily an experimental branch of science. Nevertheless, the physical chemist, as well as the mathematical physicist, will find much here of deep interest, and of the highest importance. This is true of the chapters which treat of thermochemistry, and especially of those which deal with the conditions of equilibrium. The unusually clear method of presentation found in the works of Duhem, commends them to all who are interested in that field in which he is so well known. H. C. J.

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[1] E. Bourquelot: J. Pharm. Chim. (6), **3**, 390.

[2] J. Grüss: Wchschr. Branerei, 1895, 1257.

[3] J. Grüss: Berl. Pharm. Ges., **5**, 258.

ELEKTROCHEMISCHE UEBUNGSAUFGABEN. Für das Praktikum sowie zum Selbstunterricht. Zusammengestellt von Dr. Felix Oettel. Mit 20 Holzschnitten im Texte. Wilhelm Knapp. Halle A. S. 1897. pp. 53.

After discussing the forms of apparatus which are best adapted to obtaining and measuring the current used in effecting electrolytic decompositions, a number of experiments are described. Among these are the electrolysis of hydrochloric acid, the electrolytic precipitations of copper, and the formation of persulphuric acid by the electrolysis of sulphuric acid.

The last, and perhaps the most interesting chapter, is on the decomposition of certain organic substances by the current. The author states in his preface that he owes this chapter to Dr. K. Elbs. It deals with the electrolytic decomposition of sodium acetate into sodium hydroxide, hydrogen, carbon dioxide and ethane; the formation of azobenzene, hydrazobenzene, *p*-amidophenol, or *p*-amidophenolsulphonic acid, by the action of the current on nitrobenzene under different conditions, using different solvents for the nitrobenzene; also the oxidation of paranitrotoluene to paranitrobenzyl alcohol, and the formation of iodoform from a solution containing sodium carbonate, potassium iodide, water, and alcohol. H. C. J.

THEORIE UND PRAXIS DER ANALYTISCHEN ELEKTROLYSE DER METALLE. Von Dr. phil. BERNHARD NEUMANN, Assistant für Hüttenkunde an der Kgl. techn. Hochschule zur Aachen.

The publication of this book is additional evidence that electrolytic methods are rapidly gaining a front rank in analytical chemistry. It is in technical establishments, especially where many analyses are demanded, that these new methods have won due recognition and greatest favor, because of their rapidity, neatness and accuracy.

The purpose of the present volume is to present the practical chemist with those electrolytic methods, which experience has shown to be the best.

It also contains concise, but complete, chapters on the more recent theories of electrolysis, details as to the best sources of electric energy, the measurement and control of the current, and a minute description of the various apparatus used in electrochemical analysis, with directions as to its proper arrangement. Much stress is laid on the important part played by current density in the separation of metals. Indeed, this constitutes a reason in the mind of the author for the preparation and publication of his book.

The chapters relating to the determination of the individual metals, as well as their separation, are quite exhaustive. In this connection it is interesting to note that the author prefers the precipitation of copper from a nitric or sulphuric acid solution, rather than from its double oxalate solution; that zinc is best precipitated from its double cyanide solution, and that the latter solution is also given preference (and rightly) in estimating cadmium, mercury, gold, silver, etc., although the reviewer cannot concur with the statement made on p. 140 that an ammoniacal solution of silver phosphate yields "ungenügende Resultate," for he has frequently observed the contrary. The methods offered for the determination of manganese, while affording good results, are not likely to replace, in iron laboratories at least, the simpler titration methods now in use for this metal.

Under separations the oxalate method is used for copper and iron, notwithstanding "sie giebt nicht immer die gewünschten Resultate." A solution of these metals, containing free sulphuric acid, is best for this purpose, and also for the separation of copper from zinc, manganese, nickel and cobalt, a form of solution first used in 1864 by Gibbs for the separation of copper from nickel.

The author recognizes the fact that double cyanide solutions lend themselves to the successful separation of more metals than any other form of solution, and accordingly recommends them, and describes their proper conditions in detail.

The literature references are numerous. Occasional errors may be detected in them; *e. g.*, *Moore* for *Muhr*, on pp. 130, 151.

However, the little volume is a valuable addition to existing electrochemical works, and its author is entitled to much credit for his labors, as well as for the disinterested but generous consideration of the works of others. E. F. SMITH.

LE FOUR ÉLECTRIQUE. Par M. HENRI MOISSAN, de l'Institut. Paris: G. Steinheil. 1897. 385 pp. Large octavo. Price, 15 francs.

Those who have not followed Prof. Moissan's work for the last five years, would not suspect from the title of this book that it was work of fundamental importance to chemistry. Yet it is this, and more. The work which it chronicles in detail is doubtless the most noteworthy contribution to inorganic chemistry since the discovery of the Periodic Law. The book demands careful study from every chemist; study which is made easy by the beauty and clearness of Moissan's style. It is not possible in a brief review to do more than refer to the chief points of interest, yet a condensed extract from the preface must find place. Moissan says:

"The study of the fluorides of phosphorus led me, after many trials and researches, to the isolation of fluorine. When I had learned to manipulate this element, I thought of utilizing its reactive energy in the reproduction of crystallized carbon. I first showed that two gaseous fluorides of carbon could be easily made, but the pyrogenic decomposition of these gases yielded only lampblack. Though these fluorides did not give the desired result, they led me to take up the systematic study of the three varieties of carbon, and to seek methods of transforming them. Recognizing that pressure was needed to make carbon crystallize, I made use of the increase of volume of cast-iron at the moment of passage from the liquid to the solid state to obtain very high pressure. This reaction occurs at about 1000°, but as I had to dissolve much carbon in the fused iron, I was compelled to heat this metal to a very high temperature. Hence the invention of my electric furnace. I was thus led to construct a laboratory apparatus which can accommodate itself to all conditions of research. I believe it to be simple and convenient. Certainly it has been of great help to me in the reproduction of the diamond, and has also permitted me to extend our knowledge of chemistry at high temperatures. This volume contains the results obtained by use of this apparatus."

The reviewer refuses to mar the eloquence of the last clause of the preface by translation; it must be given in the original.

"Mais ce que je ne puis rendre dans ces chapitres successifs, c'est la joie que j'ai éprouvée à poursuivre toutes ces découvertes. Marcher dans un sillon nouvellement ouvert, se sentir les coudées franches et voir de toutes côtés surgir de nouveaux sugets d'étude, procure un bonheur, que ceux-là seuls, qui ont éprouvé l'âpre plaisir de la recherche peuvent entièrement comprendre."

The book is divided into four chapters. The first treats of the different forms of electric furnace employed; the temperature obtainable is estimated at 3500°. The only reason that this temperature is the limit is that no material known suitable for furnace or crucible can resist this temperature more than a few minutes, and would be instantly destroyed by increased heat. The temperature seems steadily to increase with intensity of current. Then follows a study of the crystallization of metallic oxides, proving that this can be effected by simple heat, which gives a vapor-tension to the fusing oxide favorable to crystallization. For lime the temperature required is about 2000°; for magnesia, higher; copper oxide is dissociated into oxygen and copper; many oxides are studied. An account of fusion and volatilization of refractory substances follows. Substances like magnesium pyrophosphate and asbestos are volatilized with complete dissociation; among many volatilized elements, platinum, uranium, silicon, and carbon may be mentioned. The most refractory oxides are volatilized and dissociated, but under proper conditions, in place of the substances hitherto known to chemists as refractory, new classes of binary compounds are formed which are more or less stable at still higher temperatures. These are the nitrides, borides, silicides, and especially the carbides.

The second chapter is a long and detailed, but fascinating, study of the element carbon in its three chief forms of amorphous carbon, graphite, diamond, and their many sub-forms, tracing the successive polymerization of this element from the simpler polymer in the form of amorphous carbon produced at ordinary temperature and pressure, to the complex polymers formed at high temperatures and pressures as the crystalline graphites or as diamond. This chapter, of course, includes a full description of the successful experiments in reproducing the diamond, which have made Moissan's name so familiar to the public.

The author devotes the third chapter to the preparation of elements in the electric furnace. He prepares chromium, manganese, molybdenum, tungsten, uranium, vanadium, zirconium, titanium, silicium, and aluminium—several for the first time pure—and gives a careful study of the properties and reactions of the single elements, with details of the methods of analysis pursued.

The fourth chapter is a study of the metallic carbides, borides, and silicides. It is impossible in a brief review even to sketch this field, where everything is new. Suffice it to say that Moissan proves that the binary compounds of the metals familiar to us as stable compounds under existing conditions; *i. e.*, the oxides, sulphides, chlorides, etc., cannot exist at high temperatures, but are decomposed, giving place to other binary compounds readily formed under these conditions, and resisting in greater or less degree much higher temperatures without decomposition. In exactly the same sense that copper sulphide is a substituted sulphuretted hydrogen, salt a substituted hydrochloric acid, quick-lime a substituted water, the nitrides are substituted ammonias, the carbides substituted hydrocarbons, the silicides substituted hydrogen silicide, the borides substituted hydrogen boride. Many of these substances indeed yield, by simple contact with water at ordinary temperatures, the hydride from which they are derived. It may suffice to mention as examples the well-known calcium carbide or, more accurately, acetylide, which yields with water pure acetylene and calcium hydroxide; the aluminium carbide or methide, which yields pure methane and aluminium hydroxide:

$$Al_4C_3 + 12H_2O = 3CH_4 + 4Al(OH)_3;$$

lithium nitride, which yields ammonia and lithium hydroxide:

$$NLi_3 + 3H_2O = NH_3 + 3LiOH.$$

Certain of the metallic carbides are not simple substances like these, but when decomposed yield mixtures of different hydrocarbons. On this fact Moissan bases his theory of the origin of natural gas and petroleum. A few pages are given to this theory. Those who are familiar with the theories and the work of Mendeléeff, Engler, and others, on this subject, will perhaps agree with the reviewer in thinking that this previous work harmonizes with and confirms Moissan's theory.

The light which Moissan's work throws on the chemistry of the stars, on the condition of our earth when its temperature was very high, and on the chemical changes which took place when the earth's crust assumed its present condition, must occur to every thoughtful reader, and are briefly discussed by the author.

In conclusion the reviewer would emphatically urge that no teacher should consider himself fitted to instruct in inorganic chemistry to-day, who has not either read this book, or the author's single articles, which have appeared during the last five years in the *Comptes Rendus*, and, in complete form, in the *Annales de Chimie et de Physique* during the years 1895–96.

It is, of course, easier and more profitable to follow the trend of the author's thoughts in the book than in the single articles. Every chemical library should have a copy of this work. Every student reading it will lay it down at the close with the same feeling of admiration for the author's genius and indomitable patience and skill in research, which the reviewer has felt in increasing degree in the study of the single articles during the last five years, and especially on reading this volume.

EDWARD RENOUF.

Correction: Vol. XIX, p. 417. *For* "Lafayette B. Wendel" *read* "Lafayette B. Mendel."

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VOL. XIX. AUGUST, 1897. No. 8.

AMERICAN
CHEMICAL JOURNAL.

Contributions from the Chemical Laboratory of Harvard College.

BY HENRY B. HILL.

XCIX.—ON THE OXIMES OF MUCOPHENOXYCHLORIC AND MUCOPHENOXYBROMIC ACIDS.

BY JOHN A. WIDTSOE.

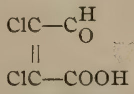
C.—ON THE ACTION OF ALUMINIC CHLORIDE AND BENZOL UPON MUCOCHLORYL CHLORIDE, MUCOBROMYL BROMIDE, AND THE CORRESPONDING ACIDS.

BY FREDERICK L. DUNLAP.

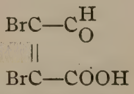
INTRODUCTION.

BY HENRY B. HILL.

Several years ago Hill and Cornelison[1] found that mucochloric and mucobromic acids yielded with hydroxylamine oximes of perfectly normal character, while the bromanhydrides of these acids could easily be converted, by reduction, into the corresponding substituted crotonolactones. The formation of oximes indicated that the acids in question contained the aldehyde group, and that their structure corresponded to the formulæ



$$\begin{array}{l} \mathrm{ClC{-}C^{H}_{O}} \\ \;\| \\ \mathrm{ClC{-}COOH} \end{array}$$



$$\begin{array}{l} \mathrm{BrC{-}C^{H}_{O}} \\ \;\| \\ \mathrm{BrC{-}COOH} \end{array}$$

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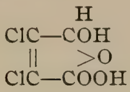
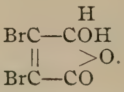
[1] This JOURNAL, **16**, 188, 277; Proc. Amer. Acad., **29**, 1.

while the ready reduction of the bromanhydrides to crotonolactones showed with equal probability that the formulæ of these acids were



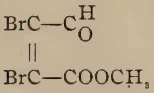
$$\begin{array}{l} \qquad\quad H \\ ClC{-}COH \\ \;\; \| \qquad >O \\ ClC{-}COOH \end{array}$$



$$\begin{array}{l} \qquad\quad H \\ BrC{-}COH \\ \;\; \| \qquad >O. \\ BrC{-}CO \end{array}$$

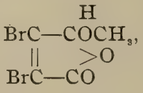
These two acids, therefore, showed, like the orthoaldehyde acids of the aromatic series investigated by Lieberman, Allendorf, Racine, Perkin, and others, the behavior ordinarily described by the term tautomerism.

Hill and Cornelison suggested the possibility of discriminating between the two forms for the methyl ester of mucobromic acid,



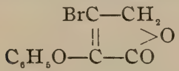
$$\begin{array}{l} BrC{-}C^{H}_{O} \\ \;\; \| \\ BrC{-}COOCH_3 \end{array}$$

and

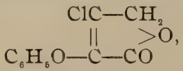


$$\begin{array}{l} \qquad\qquad H \\ BrC{-}COCH_3, \\ \;\; \| \qquad >O \\ BrC{-}CO \end{array}$$

in that the first form would probably react with hydroxylamine as readily as the free acid, while the second form would yield with more difficulty a derivative of the ordinary aldoxime. The experiments which they made with mucobromic and mucochloric acids, and with their methyl esters showed that while the reaction with the free acids was completed in a very short time, little or no product could be obtained from the esters even on long standing. It seemed desirable to determine whether other acids of this series would show the same difference in behavior when compared with their esters, and Mr. J. A. Widtsoe, therefore, undertook the study of mucophenoxybromic and mucophenoxychloric acids in this direction. Hill and Cornelison had reduced the bromanhydrides of these acids to the corresponding lactones,



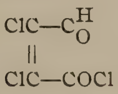
$$\begin{array}{l} \qquad\quad BrC{-}CH_2 \\ \qquad\quad\;\; \| \qquad >O \\ C_6H_5O{-}C{-}CO \end{array}$$



$$\begin{array}{l} \qquad\quad ClC{-}CH_2 \\ \qquad\quad\;\; \| \qquad >O, \\ C_6H_5O{-}C{-}CO \end{array}$$

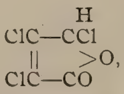
and had prepared also their oximes; but they had made no study of their esters. In the course of his investigations Mr. Widtsoe showed that the methyl esters of these acids reacted promptly with hydroxylamine, and gave at once bodies which were identical with the esters made from the oximes through the action of methyl iodide upon their silver salts. The marked differences in behavior which had been shown by mucobromic or mucochloric acid and their methyl esters, disappeared as soon as one atom of halogen was replaced by the phenoxy group. It is not easy to account for this radical change in behavior, but in any case the prompt reaction with hydroxylamine is to be taken as evidence that these esters contain the aldehyde group. Mr. Widtsoe also made a more extended study of the oximes in question and their derivatives.

Although the conversion of mucobromic and mucochloric acids through their bromanhydrides into substituted crotonolactones, found its most simple explanation in the assumption that these acids were themselves oxylactones, in view of the general interest attaching to the question of the structure of the δ-aldehyde and δ-ketone acids, it seemed desirable to secure further experimental evidence through reactions of an entirely different character. It is well known that acid chloranhydrides of normal form yield, when treated according to the method of Friedel and Crafts, with aluminic chloride and benzol ketones by the replacement of the chlorine of chloranhydride by the phenyl group. It seemed possible that this reaction might give the means of distinguishing between the two structural forms



$$\begin{array}{l} \mathrm{ClC{-}C}^{\mathrm{H}}_{\mathrm{O}} \\ \;\| \\ \mathrm{ClC{-}COCl} \end{array}$$

and

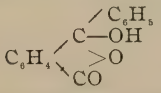


$$\begin{array}{l} \qquad\;\;\mathrm{H} \\ \mathrm{ClC{-}CCl} \\ \;\|\qquad >\mathrm{O}, \\ \mathrm{ClC{-}CO} \end{array}$$

since the first body should give an aldehyde phenylketone, while the second should yield a dichlordiphenylcrotonic acid. In the same way mucochloric acid itself, when treated with benzol and aluminic chloride, might also yield dichlordiphenylcrotonic acid, if it is an oxylactone, while an aldehyde acid of ordinary form could hardly give such a product.

Mr. F. L. Dunlap undertook the experimental investigation of these reactions, and found that dichlordiphenylcrotonic acid could be formed with satisfactory yield when mucochloryl chloride or mucochloric acid was heated in benzol solution with aluminic chloride; with mucobromic acid the analogous dibromdiphenylcrotonic acid was formed. The constitution of these acids was determined with precision by their conversion through oxidation into diphenylacetic acid.

These results apparently warrant the conclusion that mucochloric acid and its chloranhydride have the lactone structure. If the aldehyde formula is adopted the formation of the dichlorphenylcrotonic acid in either case can be explained only by the assumption that the aldehyde group is first attacked with the addition of benzol. As far as I am aware, but one similar reaction has been observed. In 1881, v. Pechmann[1] showed that *o*-benzoylbenzoic acid could be converted into phthalophenone by the action of aluminic chloride and benzol; a better yield was obtained in the same way from *o*-benzoylbenzoic acetic anhydride. While v. Pechmann notes that the latter reaction is anomalous in that acid anhydrides were shown by Friedel and Crafts to yield ketones, he remarks that the difference is due to the great reactive-power of the ketone group of the benzoylbenzoic acid. The conclusion could quite as fairly be drawn, however, from v. Pechmann's observations, that the benzoylbenzoic acid and its anhydride with acetic acid had the structure



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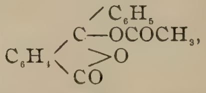
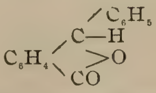


The reaction then becomes perfectly normal. It should be noted in this connection that, according to the observations of Gresly,[2] the anhydride of *o*-benzhydrylbenzoic acid, phenylphthalid,



by the action of aluminic chloride and benzol is converted into triphenylmethanecarboxylic acid, although the reaction with phthalic anhydride apparently ends with the formation of phthalophenone.

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[1] Ber. d. chem. Ges., **14**, 1865.

[2] Ann. chem. (Liebig), **234**, 241.

THE OXIMES OF MUCOPHENOXYBROMIC AND MUCOPHENOXYCHLORIC ACIDS.[1]

BY JOHN A. WIDTSOE.

Mucophenoxybromic Acid.

Mucophenoxybromoxime was first made by Hill and Cornelison,[2] and their method has been followed in the preparation of the material needed for this work. It has been found advantageous, however, to diminish the amount of the solvent which they recommend. Instead of dissolving the mucophenoxybromic acid in twenty times its weight of 50 per cent. methyl alcohol, a better yield was obtained when 2 cc. of methyl alcohol of this strength was used for each gram of the acid. Under these conditions the yield was nearly quantitative.

Silver Salt of Mucophenoxybromoxime, $C_4H_2(OC_6H_5)Br NO_3Ag$.—This salt was thrown down as an amorphous, voluminous precipitate when argentic nitrate was added to a neutral solution of the oxime in pure potassic hydrate. It may also be prepared by mixing alcoholic solutions of argentic nitrate and mucophenoxybromoxime, but, as it is somewhat soluble in alcohol, the yield is not satisfactory.

I. 0.3011 gram salt gave with HBr 0.1453 gram AgBr.

II. 0.2886 gram salt gave when heated with HNO_3 0.1381 gram AgBr.

	Calculated for $C_4H_2(OC_6H_5)BrNO_3Ag$.	Found.	
		I.	II.
Ag	27.48	27.72	....
Br	20.35	....	20.36

Methyl Ester of Mucophenoxybromoxime, $C_4H_2(OC_6H_5)Br NO_3CH_3$.—This body could not be made from the oxime by the action of methyl alcohol; the oxime remained unaltered, was converted into its anhydride or the corresponding imide according to the conditions employed. The methyl ester could be prepared, however, by the action of methyl iodide upon the silver salt of mucophenoxybromoxime. The best yield was obtained when the silver salt and methyl iodide were heated with a return-condenser for about an hour. The ester was then taken up with ether, and the residue left by the evaporation of the ethereal solution recrystallized from benzol.

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[1] The work described in the following paper was presented in the form of a thesis to the Faculty of Arts and Sciences of Harvard University, in May, 1894, by John A. Widtsoe, then candidate for the degree of Bachelor of Science.

[2] This JOURNAL, **16**, 306; Proc. Amer. Acad., **29**, 53.

I. 0.2156 gram substance gave 0.3472 gram CO_2 and 0.0586 gram H_2O.

II. 0.2446 gram substance gave 0.1506 gram AgBr.

III. 0.2646 gram substance gave 10.4 cc. moist nitrogen at 19° and under a pressure of 778 mm.

	Calculated for $C_4H_2(OC_6H_5)BrNO_3CH_3$.	Found. I.	II.	III.
C	44.00	43.93	....	....
H	3.33	3.02	....	....
Br	26.67	....	26.20	....
N	4.67	....	....	4.62

The methyl ester of the mucophenoxybromoxime is insoluble in water, carbonic disulphide, or ligroïn ; it is sparingly soluble in ether, methyl alcohol, or chloroform ; in hot acetone, glacial acetic acid, benzol, or toluol it dissolves more freely, and from the latter it crystallizes well on cooling. It then melts, when heated in the usual way, from 150°–165°, while the melting-point determined by dipping the capillary tube into the heated bath is approximately 168°–170°. It is saponified by sodic or potassic hydrate, while aqueous ammonic hydrate dissolves it only on long standing. In this case a brown resinous body was obtained which has not been further studied. When the ester is treated with hydrochloric acid in alcoholic solution it gives the mucophenoxybromoxime anhydride, and the anhydride is also slowly formed when the ester is suspended in a mixture of acetic acid and acetic anhydride saturated with hydrochloric acid gas. When the ester is boiled with alcohol, slightly acidified with hydrochloric acid, phenoxybrommaleïnimide is formed. A body in all respects identical with the ester first described is formed when hydroxylamine hydrochlorate acts upon methyl mucophenoxybromate in alcoholic solution.

Methyl Mucophenoxybromate, $C_4H(OC_6H_5)BrO_3CH_3$.—Argentic mucophenoxybromate is easily made by adding argentic nitrate to a solution of the potassium salt. The well-dried salt reacts at ordinary temperatures with methyl iodide with the evolution of heat. The ester thus formed was extracted with ether and recrystallized from ligroïn.

I. 0.2562 gram substance gave 0.4306 gram CO_2 and 0.0749 gram H_2O.

II. 0.2454 gram substance gave 0.1640 gram AgBr.

	Calculated for $C_4H(OC_6H_5)BrO_3CH_3$.	Found.	
		I.	II.
C	46.33	45.86	....
H	3.13	3.25	....
Br	28.07	....	28.44

Methyl mucophenoxybromate forms radiating needles, which melt at 75°–76°. It is readily soluble in alcohol, ether, chloroform, carbonic disulphide, benzol, toluol, or glacial acetic acid. It is sparingly soluble in cold ligroïn, but dissolves more freely on heating, and crystallizes well as the solution cools. It is quickly decomposed when exposed to direct sunlight, and even in diffused light it decomposes when exposed to the air for a few weeks; in a tightly stoppered bottle it softens and turns yellow in the course of a few months.

Hydroxylamine Hydrochlorate with Methyl Mucophenoxybromate.—When a little more than the calculated amount of hydroxylamine hydrochlorate in aqueous solution is added to an alcoholic solution of methyl mucophenoxybromate, the oxime ester is immediately thrown down. The substance thus precipitated, when recrystallized from benzol, gave the following results:

I. 0.2743 gram substance gave 0.4444 gram CO_2 and 0.0743 gram H_2O.

II. 0.2224 gram substance gave 0.1364 gram AgBr.

III. 0.3071 gram substance gave 12.6 cc. moist nitrogen at 21° and under a pressure of 762 mm.

	Calculated for $C_4H_2(OC_6H_5)BrNO_3CH_3$.		Found.	
		I.	II.	III.
C	44.00	44.18	....	....
H	3.33	3.01	....	....
Br	26.67	....	26.10	....
N	4.67	....	....	4.68

The physical properties of this substance agree in every respect with those of the ester made from the silver salt of the mucophenoxybromoxime by the action of methyl iodide. When slowly heated it melted as low as 150°, but by more rapid heating the melting-point could be raised to 165°. By dipping the capillary tube into the heated bath its melting-point was found to be approximately 168°–170°.

Ethyl Ester of Mucophenoxybromoxime, $C_4H_2(OC_6H_5)BrNO_3C_2H_5$.—Although the methyl ester could not be formed by the action of methyl alcohol upon the mucophenoxybromoxime, if the oxime was heated for a short time with absolute alcohol, to which a small amount of hydrochloric acid had been added, the ethyl ester was formed without difficulty. The same body was also formed by the action of ethyl iodide upon the silver salt of the oxime. At the boiling-point of the ethyl iodide the reaction is soon complete, and the product may be extracted with ether.

I. 0.2112 gram substance prepared from the silver salt gave 0.3568 gram CO_2 and 0.0684 gram H_2O.

II. 0.2177 gram substance prepared from the silver salt gave 0.1302 gram AgBr.

III. 0.2556 gram substance prepared from the oxime with alcohol gave 0.1533 gram AgBr.

	Calculated for $C_4H_2(OC_6H_5)BrNO_3C_2H_5$.	Found. I.	 II.	 III.
C	45.87	46.06	....	....
H	3.82	3.60	....	....
Br	25.48	....	25.45	25.53

The ethyl ester of mucophenoxybromoxime is readily soluble in alcohol; more sparingly soluble in chloroform, benzol, toluol, or glacial acetic acetic acid; it is very sparingly soluble even in boiling ligroïn. It crystallizes from water or dilute alcohol in beautiful flat, silky needles, which melt rather sharply at 122°–124°.

Mucophenoxybromoxime Anhydride, $C_4H(OC_6H_5)BrNO_2$.—When hydrochloric acid gas is passed into a concentrated solution of mucophenoxybromoxime in methyl or ethyl alcohol, and the temperature of the liquid is not allowed to rise above 20°, a crystalline precipitate of oxime anhydride is formed in the course of a few minutes; more of the anhydride may be obtained from the filtrate by the immediate addition of water. The same body may be obtained in pure condition by passing gaseous hydrochloric acid into a solution of oxime in glacial acetic acid, to which about ten per cent. of acetic anhydride has been added. After the solution has stood over night, water throws down the anhydride nearly pure. For analysis it was recrystallized from benzol.

I. 0.2528 gram substance gave 0.4165 gram CO_2 and 0.0556 gram H_2O.

II. 0.2246 gram substance gave 0.1573 gram AgBr.

III. 0.2149 gram substance gave 0.1521 gram AgBr.

IV. 0.2460 gram substance gave 12 cc. moist nitrogen at 20° and under a pressure of 753 mm.

	Calculated for $C_4H(OC_6H_5)BrNO_2$.	Found. I.	II.	III.	IV.
C	44.78	44.92	....	....	....
H	2.24	2.44	....	....	....
Br	29.85	....	29.81	30.12	....
N	5.22	....	....	....	5.53

Mucophenoxybromoxime anhydride is insoluble in water, sparingly soluble in chloroform or carbonic disulphide, readily soluble in methyl alcohol or glacial acetic acid; from benzol it crystallizes in pearly white scales. When heated in ordinary fashion the body melts at 121°, but on rapid heating the melting-point is 124°–126°. It dissolves slowly in a dilute solution of sodic hydrate, and the immediate addition of acid throws down a small quantity of a body melting at 140°–144°, which is without doubt the phenoxybrommaleïnimide. From the solution may then be extracted, by ether, a colorless acid, which, after sublimation, melted at 90°–91°, the melting-point of phenoxybrommaleic anhydride.

Phenoxybrommaleïnimide, $C_4H(OC_6H_5)BrNO_2$.—Although most of the oximes of similar structure can be converted by heat through their anhydrides into the imides, the phenoxybrommaleïnimide apparently cannot be made in this way. If mucophenoxybromoxime anhydride is suspended in a small amount of methyl or ethyl alcohol saturated with gaseous hydrochloric acid it slowly goes into solution, and the addition of water to this solution then precipitates phenoxybrommaleïnimide. The oxime may also be converted into the imide by heating its alcoholic solution for several hours at 100°, or by boiling for some time its solution in methyl alcohol after the addition of a few drops of concentrated hydrochloric acid. By following the last method the imide is obtained, combined with one molecule of methyl alcohol. The substance was recrystallized from benzol for analysis.

I. 0.3174 gram substance gave 0.5244 gram CO_2 and 0.0634 gram H_2O.

II. 0.1992 gram substance gave 0.1372 gram AgBr.

III. 0.1579 gram substance gave 0.1089 gram AgBr.

IV. 0.2861 gram substance gave 0.1971 gram AgBr.

V. 0.2098 gram substance gave 9.3 cc. moist nitrogen at 19° and under a pressure of 765 mm.

	Calculated for $C_4H(OC_6H_5)BrNO_2$.	Found. I.	II.	III.	IV.	V.
C	44.78	45.04	....	....	....	....
H	2.24	2.22	....	....	....	....
Br	29.85	....	29.31	29.36	29.32	....
N	5.23	....	....	....	....	5.13

The phenoxybrommaleïnimide crystallizes in large, colorless plates, which melt at 144°–145° when heated at ordinary speed; by dipping the capillary tube into the heated bath the melting-point was found to be 148°–150°. The crude product always has a faint pink color, which cannot be removed by recrystallization from benzol, but which disappears after several recrystallizations from boiling water. The imide dissolves readily in acetone or glacial acetic acid; it is sparingly soluble in chloroform, and nearly insoluble in ligroïn or carbonic disulphide. It dissolves readily in dilute solutions of the alkaline hydrates, and the immediate addition of acid reprecipitates it in part unchanged. After the lapse of a short time the alkaline solution contains phenoxybrommaleïc acid, which was identified by the melting-point 90°–91° of the sublimed anhydride. When the imide is boiled for several hours with water the same change takes place.

It has already been mentioned that when the phenoxybrommaleïnimide is prepared by boiling the oxime with methyl alcohol, to which a few drops of hydrochloric acid are added, the imide thrown down with water contains one molecule of methyl alcohol. The same product can be made by boiling the imide with methyl alcohol and hydrochloric acid. The body crystallizes from benzol in long, coarse needles, which lose their crystal alcohol readily at 100°. When dissolved in hot water the compound is also immediately broken up, and the ordinary imide crystallizes out as the solution cools.

I. 0.3148 gram substance gave 0.5076 gram CO_2 and 0.0963 gram H_2O.

II. 0.2233 gram substance gave 0.1372 gram AgBr.

III. 0.2019 gram substance gave 0.1267 gram AgBr.

IV. 0.2472 gram substance gave 10.0 cc. moist nitrogen at 20° and under a pressure of 752 mm.

V. 0.1651 gram substance lost at 90°–100° 0.0172 gram.

	Calculated for	Found.				
	$C_4H(OC_6H_5)BrNO_2.CH_3OH$.	I.	II.	III.	IV.	V.
C	44.00	43.97	....	....	....	....
H	3.33	3.40	....	....	....	....
Br	26.67	....	26.14	26.71	....	....
N	4.67	....	....	....	4.58	....
CH_3OH	10.67	....	....	....	....	10.42

Silver Salt of Phenoxybrommaleïnimide, $C_6(OC_6H_5)BrNO_2Ag$.—When alcoholic solutions of phenoxybrommaleïnimide and argentic nitrate are mixed together no reaction takes place even after the lapse of many hours. The addition of alcoholic ammonia, however, immediately throws down small, yellowish, granular crystals of the silver salt of the imide.

I. 0.2341 gram substance, when heated with nitric acid, gave 0.1183 gram AgBr.

II. 0.2477 gram substance, precipitated with hydrobromic acid, gave 0.1230 gram AgBr.

	Calculated for	Found.	
	$C_4(OC_6H_5)BrNO_2Ag$.	I.	II.
Br	21.34	21.51	....
Ag	28.80	....	28.52

Mucophenoxychloric Acid.

Methyl Ester of Mucophenoxychloroxime, $C_4H_2(OC_6H_5)ClNO_3$

CH_3.—The ester could not be made directly from the oxime by the action of methyl alcohol; it could be made, however, by the action of methyl iodide upon the silver salt of the oxime. The reaction was soon finished at 40°; the ester was then extracted with ether and recrystallized from benzol.

I. 0.2383 gram substance gave 0.4509 gram CO_2 and 0.0770 gram H_2O.

II. 0.2599 gram substance gave 0.1444 gram AgCl.

III. 0.2752 gram substance gave 13.3 cc. moist nitrogen at 23° and under a pressure of 749 mm.

	Calculated for $C_4H_2(OC_6H_5)ClNO_3CH_3$.	Found. I.	II.	III.
C	51.66	51.60	....	....
H	3.91	3.59	....	....
Cl	13.90	....	13.74	....
N	5.48	....	....	5.36

The methyl ester of the mucophenoxychloroxime forms long, silky needles, which are insoluble in water, sparingly soluble in carbonic disulphide or cold chloroform. The body dissolves freely in hot benzol or toluol, and crystallizes well on cooling. The melting-point varies with the rate of heating; when heated in the ordinary way it melts at 156°–160°, but on dipping the substance into the heated bath its melting-point seems to be 162°–166°. This ester may also be made by the action of hydroxylamine hydrochlorate upon methyl mucophenoxychlorate.

Methyl Mucophenoxychlorate, $C_4H(OC_6H_5)ClO_3CH_3$.—Methyl iodide reacts upon dry argentic mucophenoxychlorate with the evolution of heat. The methyl ester thus formed may be extracted by ether and recrystallized from ligroïn.

I. 0.1947 gram substance gave 0.3903 gram CO_2 and 0.0622 gram H_2O.

II. 0.2560 gram substance gave 0.1531 gram AgCl.

	Calculated for $C_4H(OC_6H_5)ClO_3CH_3$.	Found. I.	II.
C	54.89	54.67	....
H	3.74	3.55	....
Cl	14.76	....	14.79

Methyl mucophenoxychlorate is soluble in most of the ordinary organic solvents. From its solution in boiling ligroïn it crystallizes on cooling in clusters of radiating needles, which melt at 59°. Like the corresponding body containing bromine, it decomposes on standing.

Hydroxylamine Hydrochlorate with Methyl Mucophenoxychlorate.—When an aqueous solution containing somewhat more than the theoretical amount of hydroxylamine hydrochlorate is added to an alcoholic solution of methyl mucophenoxychlorate, the oxime of the ester is immediately thrown down. This body was in appearance and behavior identical with the ester already described as made by the action of methyl iodide upon the silver salt of the mucophenoxychloroxime. When recrystallized from benzol it also contained the proper percentage of chlorine.

0.2068 gram substance gave 0.1161 gram AgCl.

	Calculated for $C_4H_2(OC_6H_5)ClNO_3CH_3$.	Found.
Cl	13.90	13.88

Mucophenoxychloroxime Anhydride, $C_4H(OC_6H\ )ClNO_2$.—When gaseous hydrochloric acid is passed into a well-cooled solution of mucophenoxychloroxime in six or seven times its weight of methyl alcohol the solution remains clear; but, if the action is not too long continued, water throws down a voluminous precipitate of the anhydride. The same body may also be made by dissolving the oxime in glacial acetic acid mixed with 10 per cent. of acetic anhydride and saturated with hydrochloric acid gas. The mixture is allowed to stand for twenty-four hours and the anhydride then precipitated by the addition of water. For analysis the substance was recrystallized from carbonic disulphide.

I. 0.2793 gram substance gave 0.5522 gram CO_2 and 0.0621 gram H_2O.

II. 0.2111 gram substance gave 0.1362 gram AgCl.

III. 0.2781 gram substance gave 14.9 cc. moist nitrogen at 21° and under a pressure of 776 mm.

	Calculated for $C_4H(OC_6H_5)ClNO_2$.	Found. I.	II.	III.
C	53.69	53.92	....	....
H	2.68	2.47	....	....
Cl	15.88	....	15.95	....
N	6.26	....	....	6.23

Mucophenoxychloroxime anhydride is readily soluble in chloroform, benzol, toluol, or glacial acetic acid; it is sparingly soluble in carbonic disulphide, and from the hot solution it is deposited in large, flexible, pearly scales, which melt rather sharply at 96°–98°. It dissolves sparingly in boiling water, and phenoxychlormaleïnimide is deposited as the solution cools; it also dissolves slowly in dilute solutions of the alkaline hydrates.

Phenoxychlormaleïnimide, $C_4H(OC_6H_5)ClNO_2$.—Mucophenoxychloroxime anhydride slowly isomerizes in strongly acid alcoholic solution and forms the corresponding phenoxychlormaleïnimide. The imide is also formed when an alcoholic solution of the oxime is heated for several hours at 100° in a sealed tube. It may, perhaps, most conveniently be prepared by saturating a concentrated alcoholic solution of the oxime with hydrochloric acid gas and allowing the solution to stand for a day or two. For analysis the substance was recrystallized from water.

I. 0.2618 gram substance gave 0.5152 gram CO_2 and 0.0567 gram H_2O.

II. 0.1886 gram substance gave 0.1202 gram AgCl.

III. 0.2257 gram substance gave 12.4 cc. moist nitrogen at 24° and under a pressure of 756 mm.

	Calculated for $C_4H(OC_6H_5)ClNO_2$.	Found. I.	II.	III.
C	53.69	53.68	....	....
H	2.68	2.41	....	....
Cl	15.88	....	15.75	....
N	6.26	....	....	6.12

Phenoxychlormaleïnimide is readily soluble in alcohol, ether, chloroform, benzol, toluol, or glacial acetic acid, but is sparingly soluble in carbonic disulphide, and almost insoluble in ligroïn. It is sparingly soluble in cold water, more freely soluble in hot water, and, as the solution cools, it separates in clustered, flattened needles, which melt at 118°–119°. On long boiling with water it is converted into the acid ammonium salt of phenoxychlormaleïc acid. Sawyer[1] gives the melting-point of the anhydride of this acid as 97°, while the sublimed acid obtained from this imide melted at 94°–95°. The imide dissolves readily in dilute sodic hydrate, and is reprecipitated from solutions, not too dilute, by the immediate addition of acid. An alcoholic solution throws down a yellowish, granular precipitate on the addition of alcoholic solutions of argentic nitrate and ammonia. Phenoxychlormaleïnimide also combines with methyl alcohol to form a compound analogous to that formed in the same way from phenoxybrommaleïnimide.

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[1] Proc. Amer. Acad., **29**, 248.

ON THE ACTION OF ALUMINIC CHLORIDE AND BENZOL UPON MUCOCHLORYL CHLORIDE, MUCOBROMYL BROMIDE, AND THE CORRESPONDING ACIDS.[1]

BY FREDERICK L. DUNLAP.

Mucochloric Acid.

The mucochloric acid needed for this work was made by the action of manganic dioxide and hydrochloric acid upon pyromucic according to a slight modification of the method already described from this laboratory.[2] Instead of adding the manganic dioxide in calculated amount to the pyromucic acid suspended in concentrated hydrochloric acid, the pyromucic acid and manganic dioxide were intimately mixed, and the mixture was then added in four portions, at intervals of ten to fifteen minutes each, to the necessary amount of hydrochloric acid (sp. gr. 1.18). This slight modification in the process increased the yield of mucochloric acid to about 75 per cent. of the weight of pyromucic acid taken.

Mucochloryl Chloride, $C_4HCl_3O_2$.—Mucochloric acid was heated gently with somewhat more than one molecule of phosphoric pentachloride. The product was then shaken with cold water, taken up with ether, and the ethereal solution dried with calcic chloride. On evaporation of the ether a yellowish oil was obtained, which attacked vigorously the mucous membrane of the eyes and nose. This product was used without farther purification in subsequent work, although an analysis showed that the percentage of chlorine which it contained was too low.

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[1] The work described in the following paper formed a part of a thesis presented to the Faculty of Arts and Sciences of Harvard University in May, 1895, by Frederick L. Dunlap, then candidate for the degree of Doctor of Philosophy.

[2] This JOURNAL, **9**, 160, Proc. Amer. Acad., **22**, 327.

0.2684 gram substance gave 0.5899 gram AgCl.

	Calculated for $C_4HCl_3O_2$.	Found.
Cl	56.80	54.34

As mucochloryl chloride had not yet been described a portion of this crude product was submitted to fractional distillation under diminished pressure. Under a pressure of 15 mm. a product was obtained which showed the constant boiling-point 100°–101°, and which contained the required percentage of chlorine.

0.2100 gram substance gave 0.4833 AgCl.

	Calculated for $C_4HCl_3O_2$.	Found.
Cl	56.80	56.90

Dichlordiphenylcrotonic Acid, $C_4H_2Cl_2(C_6H_5)_2O_2$.—Mucochloryl chloride was dissolved in four times its weight of benzol, diluted with twice its volume of carbonic disulphide, and anhydrous aluminic chloride was then added to the solution. The evolution of hydrochloric acid was at once noticeable, and for the completion of the reaction it was found necessary to add an amount of aluminic chloride equal to two or three times the weight of mucochloryl chloride taken. In order to accelerate the action, the flask was heated with a return-condenser; exposure to the direct sunlight also appeared to facilitate the reaction. After heating from thirty to forty hours the evolution of hydrochloric acid ceased, and the contents of the flask were then poured into dilute hydrochloric acid. The carbonic disulphide and benzol were driven off by warming the whole upon the water-bath, and the heat was continued until the oily viscous liquid, which was first obtained, solidified. The crystalline product was then boiled with water to remove all unaltered mucochloryl chloride or mucochloric acid, and the dark-colored residue, after thorough drying, extracted with cold benzol. The main product of the reaction is sparingly soluble in cold benzol, while the tarry by-products are to a great extent removed. The substance is finally purified by repeated recrystallization from glacial acetic acid or from ligroïn. This same body may also be made more conveniently by the action of aluminic chloride and benzol upon mucochloric acid itself. The method of preparation and purification is identical with that just described, except that but half of the amount of aluminic chloride given above is needed to complete the reaction.

I. 0.1991 gram substance made from mucochloryl chloride gave 0.4596 gram CO_2 and 0.0730 gram H_2O.

II. 0.1887 gram substance made from mucochloryl chloride gave 0.1769 gram AgCl.

III. 0.2261 gram substance made from mucochloric acid gave 0.2125 gram AgCl.

	Calculated for $C_{16}H_{12}Cl_2O_2$.	Found. I.	II.	III.
C	62.55	62.95	....	....
H	3.91	4.07	....	....
Cl	23.13	....	23.17	23.24

Dichlordiphenylcrotonic acid is insoluble in water, readily soluble in ether or acetone, somewhat more sparingly soluble in alcohol or chloroform; it is sparingly soluble in cold benzol or carbonic disulphide, although it dissolves more freely on heating. From boiling ligroïn it crystallizes in short, colorless, frequently clustered prisms, which melt at 152°. It dissolves readily in solutions of the alkalies in the cold, and these solutions yield with acids a viscous precipitate, which solidifies on standing. If the alkaline solution is heated, decomposition ensues, and a colorless oil separates. The methyl and ethyl esters of this acid appear to be liquids, but for its better characterization several of its salts were made.

Baric Dichlordiphenylcrotonate, $Ba(C_{16}H_{11}Cl_2O_2)_2.2H_2O$.—Baric chloride added to an ammoniacal solution immediately throws down the barium salt in the form of clusters of minute radiating needles. The salt is so sparingly soluble even in boiling water that it was well washed and analyzed without recrystallization.

I. 0.2346 gram air-dried salt gave 0.0686 gram $BaSO_4$.

II. 0.5250 gram air-dried salt lost at 110° 0.0234 gram H_2O.

	Calculated for $Ba(C_{16}H_{11}Cl_2O_2)_2.2H_2O$.	Found. I.	II.
Ba	17.45	17.19	....
H_2O	4.59	....	4.46

0.2222 gram anhydrous salt gave 0.0690 gram $BaSO_4$.

	Calculated for $Ba(C_{16}H_{11}Cl_2O_2)_2$.	Found.
Ba	18.29	18.25

Calcic Dichlordiphenylcrotonate, $Ca(C_{16}H_{11}Cl_2O_2)_2.2H_2O$.—This salt was made by precipitating an ammoniacal solution of the acid with calcic chloride. The microcrystalline precipitate was almost insoluble in water and was analyzed without further purification.

I. 0.1921 gram air-dried salt gave 0.0386 gram $CaSO_4$.

II. 0.3244 gram air-dried salt lost at 100° 0.0167 gram H_2O.

	Calculated for $Ca(C_{16}H_{11}Cl_2O_2)_2.2H_2O$.	Found.	
		I.	II.
Ca	5.82	5.91	....
H_2O	5.23	....	5.15

0.1832 gram salt dried at 110° gave 0.0377 gram $CaSO_4$.

	Calculated for $Ca(C_{16}H_{11}Cl_2O_2)_2$.	Found.
Ca	6.14	6.05

Oxidation of Dichlordiphenylcrotonic Acid.

Dichlordiphenylcrotonic acid was readily attacked by potassic permanganate in alkaline solution, and the reaction was studied more in detail in order to establish the structure of the acid. The acid was dissolved in an excess of sodic carbonate in dilute solution, and rather more than two-thirds of a molecule of potassic permanganate was added. The mixture was then allowed to stand at ordinary temperature for several hours until the color had disappeared. On the addition of acid to the filtered solution a yellowish, viscous mass was thrown down, which gradually solidified on standing. This crude oxidation-product, which amounted to about 30 per cent. of the weight of the acid taken, had a distinct odor of benzophenone, and gave with concentrated sulphuric acid the deep-red color described by Zinin[1] as characteristic of benzilic acid. After recrystallization from glacial acetic acid, it no longer gave this color reaction, and analysis showed that it had the percentage composition of diphenylacetic acid.

[1] Ann. Chem. (Liebig), **31**, 330.

0.1948 gram substance gave 0.5656 gram CO_2 and 0.1050 gram H_2O.

	Calculated for $C_{14}H_{12}O_2$.	Calculated for $C_{14}H_{12}O_3$.	Found.
C	79.25	73.69	79.18
H	5.66	5.26	5.99

The acid recrystallized from glacial acetic acid melted at 144°–145°, and this melting-point could not be raised by further recrystallization. The melting-point of diphenylacetic acid has been found to be somewhat higher by other observers: Jena[1] gives it as 146°, Symons and Zincke[2] as 145°–146°, while Friedel and Balsohn[3] found it to be 148°. The identity of the acid was definitely established, however, by the melting-point of its ethyl ester, 57°–58°, which agrees precisely with the observations of Symons and Zincke. When warmed with concentrated sulphuric acid it gave the greenish-yellow color described by Jena.

Reduction of Diphenyldichlorcrotonic Acid.

Diphenyldichlorcrotonic acid was dissolved in a dilute solution of sodic carbonate and an excess of a 4 per cent. sodium amalgam was added. After standing over night, the solution was decanted from the mercury and acidified. The viscous acid which separated gradually solidified on standing, and on crystallization from high-boiling ligroïn, it was obtained in clusters of small-pointed, radiating prisms. An analysis of the acid showed that its composition corresponded more nearly to that of a diphenylbutyric than a diphenylcrotonic acid.

0.2382 gram substance gave 0.6996 gram CO_2 and 0.1392 gram H_2O.

	Calculated for $C_{16}H_{16}O_2$.	Calculated for $C_{16}H_{14}O_2$.	Found.
C	80.00	80.67	80.09
H	6.67	5.88	6.49

The behavior of the acid toward bromine farther showed that it was a derivative of butyric and not of crotonic acid; when dissolved in chloroform no addition-product was formed, even after the lapse of several days. The γ-diphenylbutyric acid is readily soluble in ether, alcohol, benzol, carbonic disulphide, and glacial acetic acid, but is more sparingly soluble in chloroform ; it is insoluble in water. When crystallized from ligroïn it melts at 106°.

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[1] Ann. Chem. (Liebig), **155**, 85.

[2] Ann. Chem. (Liebig), **171**, 129.

[3] Bull. Soc. Chim., **33**, 590.

Argentic γ-Diphenylbutyrate, $AgC_{16}N_{15}O_2$.—The silver salt was made by the addition of argentic nitrate to a neutral solution of the ammonium salt. It appeared to be amorphous, and was practically insoluble in water.

0.2315 gram salt gave 0.0955 gram AgCl.

	Calculated for $AgC_{16}H_{15}O_2$.	Found.
Ag	31.13	31.06

The barium and calcium salts of the acid are amorphous.

Mucobromic Acid.

Many attempts were made to prepare the dibromdiphenylcrotonic acid by the action of aluminic chloride and benzol upon mucobromyl bromide. Although the process was modified in various ways, the product in each case was a black, resinous mass, from which no crystalline body could be isolated. When mucobromic acid, however, was substituted for the mucobromyl bromide, a satisfactory product could be obtained without difficulty.

Dibromdiphenylcrotonic Acid, $C_4H_2Br_2(C_6H_5)_2O_2$.—In preparing this acid essentially the same method was followed that has already been described for making dichlordiphenylcrotonic acid from mucochloric acid. Mucobromic acid was dissolved in five times its weight of benzol, diluted with twice its volume of carbonic disulphide ; anhydrous aluminic chloride was then added, and the solution heated with return-condenser. In order to complete the reaction, it was found necessary to add an amount of aluminic chloride equal to one and a half times the weight of the mucobromic acid taken. The dark-colored product which was obtained was purified by washing with small quantities of benzol and recrystallization from glacial acetic acid.

I. 0.1751 gram substance gave 0.3091 gram CO_2 and 0.0512 gram H_2O.

II. 0.1778 gram substance gave 0.1696 gram AgBr.

	Calculated for $C_{16}H_{12}Br_2O_2$.	Found. I.	Found. II.
C	48.49	48.15	....
H	3.03	3.25	....
Br	40.40	....	40.60

Dibromdiphenylcrotonic acid is insoluble in water; readily soluble in alcohol, ether, chloroform, or carbonic disulphide; it is more sparingly soluble in cold benzol or ligroïn, but dissolves freely on heating. From glacial acetic acid it crystallizes in clustered, pointed prisms, which melt at 146°–147.° It is decomposed by heating its alkaline solution, and throws down a colorless oil; but it may be reprecipitated unchanged from cold alkaline solutions. The ethyl ester of the acid was obtained only in the form of a liquid and was not further examined; its methyl ester and several of its salts were made.

Methyl Dibromdiphenylcrotonate, $C_{16}H_{12}Br_2O_2CH_3$.—This body could not conveniently be made by the action of gaseous hydrochloric acid upon a solution of the acid in methyl alcohol. It was prepared without difficulty, however, by heating a solution of the acid in four times its weight of methyl alcohol with the addition of concentrated sulphuric acid. The ester was precipitated with water, taken up with ether, and the ethereal solution dried with calcic chloride after thorough washing with a dilute solution of sodic carbonate. The oily residue left by the ester soon solidified, and the body was then purified by recrystallization from alcohol.

0.1883 gram substance gave 0.1730 gram AgBr.

	Calculated for $C_{16}H_{12}Br_2O_2CH_3$.	Found.
Br	39.02	39.09

Methyl dibromdiphenylcrotonate is readily soluble in ether, chloroform, benzol, or carbonic disulphide, more sparingly soluble in ligroïn. From alcohol it crystallizes in four-sided pyramids, which melt at 79°–80°.

Baric Dibromdiphenylcrotonate, $Ba(C_{16}H_{11}Br_2O_2)_2.3H_2O$.—This salt is thrown down as a microcrystalline precipitate on the addition of baric chloride to an ammoniacal solution of the acid. It is very sparingly soluble even in boiling water; it was, therefore, thoroughly washed and analyzed without further purification. At temperatures above 100° it was soon decomposed.

I. 0.2075 gram air-dried salt gave 0.0484 gram $BaSO_4$.

II. 0.4575 gram air-dried salt lost at 100° 0.0244 gram H_2O.

	Calculated for $Ba(C_{16}H_{11}Br_2O_2)_2.3H_2O$.	Found. I.	Found. II.
Ba	13.96	13.71	....
H_2O	5.50	....	5.33

0.2247 gram salt dried at 100° gave 0.0558 gram $BaSO_4$.

	Calculated for $Ba(C_{16}H_{11}Br_2O_2)_2$.	Found.
Ba	14.78	14.60

Calcic Dibromdiphenylcrotonate, $Ca(C_{16}H_{11}Br_2O_2)_2.2H_2O$.—Calcic chloride added to an ammoniacal solution of the acid immediately throws down the calcium salt in minute, clustered needles, which are very sparingly soluble even in boiling water.

I. 0.2826 gram air-dried salt gave 0.0430 gram $CaSO_4$.

II. 0.6668 gram air-dried salt lost at 110° 0.0274 gram H_2O.

	Calculated for $Ca(C_{16}H_{11}Br_2O_2)_2.2H_2O$.	Found. I.	Found. II.
Ca	4.62	4.48	....
H_2O	4.16	....	4.11

0.2480 gram salt dried at 100° gave 0.0404 gram $CaSO_4$.

	Calculated for $Ca(C_{16}H_{11}Br_2O_2)_2$.	Found.
Ca	4.82	4.79

Argentic Dibromdiphenylcrotonate, $AgC_{16}H_{11}Br_2O_2$.—The silver salt is amorphous and was made by the addition of argentic nitrate to a neutral solution of the ammonium salt.

0.2321 gram salt gave 0.0871 gram AgBr.

	Calculated for $AgC_{16}H_{11}Br_2O_2$.	Found.
Ag	21.47	21.55

Dibromdiphenyl crotonic acid is oxidized readily by potassic permanganate in alkaline solution, and yields diphenylacetic acid. The acid was not analyzed; but its identity was established by its melting-point 144°–145°, the melting-point of its ethyl ester 57°–58°, and by the characteristic color reaction with sulphuric acid. In the same way the identity of the acid formed from it by reduction was sufficiently determined by the melting-point 106°, and by comparison with the diphenylbutyric acid made from dichlordiphenylcrotonic acid.

Decomposition of Dibromdiphenylcrotonic Acid in Alkaline Solution.

The decomposition which ensues when dibromdiphenylcrotonic acid, or the corresponding body containing chlorine, is heated in alkaline solution has already been mentioned. While there could be little doubt that the colorless oil which was formed in either case was a substituted diphenylallylene, it seemed worth while to study the reaction farther. Dibromdiphenylcrotonic acid was, therefore, dissolved in a dilute solution of sodic carbonate, and the strongly alkaline solution boiled with reverse-condenser. The liquid soon became turbid with the separation of oil drops and, after the completion of the reaction, the oil was distilled over with steam, taken up with ether, and the ethereal solution dried with calcic chloride. The residue left on evaporation of the ether showed no tendency to crystallize and, as the quantity of material was necessarily limited, it was thought advisable to form at once a bromine addition-product. The oil took up bromine readily with the evolution of heat, and with due care the formation of hydrobromic acid could be prevented. The product then solidified without difficulty, and by recrystallization from ligroïn was obtained in large, clustered, oblique prisms.

0.2115 gram substance gave 0.2753 gram AgBr.

	Calculated for $C_{15}H_{11}Br_3$.	Found.
Br	55.68	55.40

This diphenylbromallylenedibromide is readily soluble in benzol, chloroform, or carbonic disulphide; it dissolves very readily in hot alcohol, but more sparingly in cold. When crystallized from ligroïn the substance melts with decomposition between 120° and 130°. It began to soften when slowly heated at 117°, and melted completely with the evolution of hydrobromic acid at 130°. With concentrated sulphuric acid it gave a dark green color.

CI.—ON CERTAIN DERIVATIVES OF BROMMALEIC AND CHLORMALEIC ACID-ALDEHYDES.

BY HENRY B. HILL AND EUGENE T. ALLEN.

In 1873 Limpricht[1] obtained by the action of aqueous bromine upon pyromucic acid a body to which he gave the formula $C_4H_4O_3$. The isolation of this body was difficult, but material enough was obtained for the necessary analyses. Since it yielded upon oxidation with argentic oxide, an acid which appeared to be fumaric acid, Limpricht concluded that this body was the half aldehyde of fumaric acid. In 1877, v. Baeyer[2] repeated this oxidation with argentic oxide and established the identity of the fumaric acid formed, but he made no attempt to isolate the acid-aldehyde itself. As far as we are aware, no further investigations have been made in this direction, although Limpricht's view of the constitution of the body in question was indirectly confirmed by Hill and Hendrixson,[3] who prepared acetacrylic acid through the same reaction from δ-methylpyromucic acid. Since the few γ-aldehyde-acids which are known are in many respects interesting, it seemed to us worth while to undertake the preparation of larger quantities of this aldehyde-acid of Limpricht, and to make a more thorough study of it.

Although we carefully followed the directions of Limpricht and afterwards modified his method in many different ways, we did not succeed in obtaining the crystalline compound which he described.[4] In every case we obtained a thick, viscous liquid, which did not solidify, even after long standing *in vacuo* over sulphuric acid. This viscous product gave the familiar reactions for aldehydes ; it reduced argentic oxide, and even Fehling's solution ; it reddened a solution of rosaniline hydrochlorate decolorized by sulphurous acid, and gave with diazobenzol sulphonate and sodium amalgam, a deep, purple color. Since we were unable to isolate the acid-aldehyde in crystalline form, we attempted to prepare some derivative of it which should be more manageable. Aniline and phenyl hydrazine readily formed insoluble products, but their physical properties did not invite further investigation. With hydroxylamine hydrochlorate, we obtained, although in small quantity, a well-defined crystalline compound, which proved to be the oxime of an acid-aldehyde containing bromine, instead of the derivative of the corresponding unsubstituted acid which we sought. Since the formation of brommaleïc acid-aldehyde had never before been observed, we determined to continue our investigations in this direction. We soon found that the yield of the brommaleïc acid-aldehyde could materially be increased by the addition of more bromine, but we did not succeed in isolating the acid itself.

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[1] Ann. Chem. (Liebig), **165**, 287.

[2] Ber. d. chem. Ges., **10**, 1362.

[3] Ber. d. chem. Ges., **23**, 452.

[4] In several cases the hydrobromic acid formed in the reaction was partially neutralized before extracting with ether. When sodic hydrate was used for this purpose, a small quantity of a yellow, pulverulent body was thrown down while the solution was still strongly acid. This substance contained no sodium, and was insoluble in all ordinary neutral solvents ; it dissolved in sodic hydrate, and was reprecipitated by the addition of acids. It dissolved also in concentrated sulphuric acid, and separated to all appearance unchanged upon the addition of water. At 185° the substance was decomposed without melting. Lack of material made an extended study of the body impracticable.

The oxime was interesting, not only in that it followed the analogy of the oximes of mucobromic and mucochloric acids, and of the orthoaldehyde-acids of the aromatic series, but also in that the corresponding derivatives of succinic acid could be made from it by addition. Furthermore, from the oxime of tribromsuccinic acid-aldehyde, through the loss of carbonic dioxide and hydrobromic acid, could be formed a derivative of acrolein. We also studied briefly the action of chlorine in aqueous solution upon pyromucic acid, and showed that chlormaleïc acid-aldehyde could thus be formed.

Brommaleïc Acid-aldoxime.

The viscous liquids which we had obtained in our attempts to prepare the aldehyde-acid of Limpricht, according to the equation,

$$C_5H_4O_3 + 2Br_2 + 2H_2O = C_4H_4O_3 + CO_2 + 4HBr,$$

were treated with small quantities of cold water, and hydroxylamine hydrochlorate added to the solution. A small amount of a crystalline oxime soon formed, which was collected, dried and purified by precipitation from ethereal solution by the addition of ligroïn. After our analyses had shown that the body contained bromine, we found that the yield could be increased very considerably by using a third molecule of bromine according to the equation:

$$C_6H_4O_3 + 3Br_2 + 2H_2O = C_4H_3BrO_3 + CO_2 + 5HBr.$$

In this case, however, we found that notable quantities of mucobromic acid were also formed. The pyromucic acid was suspended in about thirty times its weight of cold water, and three molecules of bromine slowly added from a burette with constant cooling and shaking. The first two molecules of bromine are quickly taken up, but the third enters into reaction very slowly, so that three or four days may elapse before the color of the bromine completely disappears. The colorless solution was filtered and thoroughly extracted with ether. The ethereal extract leaves on distillation a viscous residue, which does not differ in appearance from the product obtained by the action of two molecules of bromine, but on extracting this residue with successive portions of cold water, and adding to the solution hydroxylamine hydrochlorate a crude product, amounting to about 40 per cent. of the weight of the pyromucic acid taken, may be obtained. The total weight of aqueous extract should be about five times the weight, that of the hydroxylamine hydrochlorate about one quarter of the weight of pyromucic acid employed. The oxime as it separates is often mixed with more or less mucobromic acid, which under these conditions, does not react as quickly upon the hydroxylamine hydrochlorate as the brommaleïc acid-aldehyde, and sometimes also with mucobromoxime. These two impurities, however, may readily be removed by warming the crude product for a short time with a little water. Mucobromoxime is thus converted into the acid ammonium salt of dibrommaleïc acid, while the small amount of mucobromic acid remains in solution.

I. 0.3120 gram substance gave 0.2878 gram CO_2 and 0.0637 gram H_2O.

II. 0.3133 gram substance gave 0.2891 gram CO_2 and 0.0604 gram H_2O.

III. 0.1238 gram substance gave 0.1201 gram AgBr.

IV. 0.3096 gram substance gave 20.6 cc. moist nitrogen at 25°.2 and under a pressure of 752 mm.

V. 0.1888 gram substance gave 12.5 cc. moist nitrogen at 21° and under a pressure of 767 mm.

	Calculated for $C_4H_4BrNO_3$.	Found. I.	II.	III.	IV.	V.
C	24.74	25.15	25.17	....	....	....
H	2.06	2.27	2.14	....	....	....
Br	41.24	....	....	41.29	....	....
N	7.22	....	....	....	7.33	7.61

Brommaleïc acid-aldoxime crystallizes in small, stout, clustered prisms, with oblique truncations. It dissolves quite readily in alcohol, or in ether; but it is almost insoluble in chloroform, benzol, carbonic disulphide, or ligroïn. It is sparingly soluble in cold water, but dissolves more freely in boiling water; with care it may also be recrystallized from glacial acetic acid. Acetyl chloride does not react upon it. The melting-point varies with the rate at which it is heated. When the temperature is slowly raised, it melts with explosive decomposition at about 143°, but by rapid heating this point may be raised some ten degrees.

The oxime may be boiled for a long time with water without essential alteration, but at 110° in sealed tubes it is soon converted into the acid ammonium salt of brommaleïc acid. This change, although not so readily effected, is identical with that noticed by Hill and Cornelison,[1] and Sawyer,[2] in the case of several oximes derived from mucochloric or mucobromic acid, and was first observed by Liebermann[3] in studying the oxime of opianic acid. In order to identify the acid with precision, it was extracted from the acidified solution with ether, and the residue obtained by evaporation of the ether was recrystallized from small quantities of water. The white, crystalline acid, when melted at ordinary speed,[4] melted at 127°–129°, and gave the percentage of bromine required for brommaleïc acid.

0.1751 gram substance gave 0.1690 gram AgBr.

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[1] This JOURNAL, **16**, 298, 304, 306; Proc. Amer. Acad., **29**, 47, 51, 53.

[2] Proc. Amer. Acad., **29**, 248.

[3] Ber. d. chem. Ges., **19**, 2925.

[4] This JOURNAL, **10**, 422: Proc. Amer. Acad., **23**, 219.

	Calculated for $C_4H_3BrO_4$.	Found.
Br	41.03	41.09

The addition of baric hydrate to an aqueous solution of the acid threw down a sandy, granular barium salt, and the supernatant liquid was farther precipitated by the addition of alcohol. By the spontaneous evaporation of its solution, the salt was obtained in spherical aggregations of small prisms. The composition of the salt also agreed tolerably well with the formula given by Wislicenus.[1]

0.2411 gram of air-dried salt gave 0.1517 gram $BaSO_4$.

	Calculated for $BaC_4HBrO_4.2\frac{1}{2}H_2O$.	Found.
Ba	36.54	36.99

Since it was thus shown that brommaleïc acid-aldehyde was formed in considerable quantity from pyromucic acid through the action of three molecules of bromine in aqueous solution, we thought it not impossible that this acid might be isolated directly from the products of the reaction. We found, however, that this product was as unmanageable as that which we had obtained by the action of two molecules of bromine. The viscous liquids could not be brought to crystallization on standing over sulphuric acid, or after extraction with various solvents. An attempt to distil the liquid *in vacuo* brought about complete decomposition. By successive treatment with water and evaporation we succeeded in removing in crystalline form a portion of the mucobromic acid which the viscous liquid contained, but the thick mother-liquors from which no crystals separated on standing, still apparently contained a small amount of mucobromic acid. A determination of bromine in the well dried residue showed too high a percentage of bromine.

0.2961 gram substance dried over H_2SO_4 gave 0.2911 gram AgBr.

	Calculated for $C_4H_3BrO_3$.	Found.
Br	44.69	46.02

We further attempted to obtain a separation by partial neutralization. A solution, partially neutralized with baric carbonate, was extracted with ether and the residue left by evaporation of the ether carefully dried as before. A complete analysis of the preparation showed that it contained more than 20 per cent. of mucobromic acid.

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[1] Ann. Chem. (Liebig), **246**, 57.

I. 0.6359 gram substance dried over H_2SO_4 gave 0.5820 gram CO_2 and 0.1000 gram H_2O.

II. 0.2668 gram substance gave 0.3046 gram AgBr.

	Calculaled for $C_4H_3BrO_3$.	Calculated for $C_4H_2Br_2O_3$.	Found. I.	II.
C	26.81	18.60	24.95	....
H	1.64	0.77	1.75	....
Br	44.69	62.02	....	48.60

For the better characterization of the brommaleïc acid-aldoxime, we have prepared several of the salts.

Barium Salt of Brommaleïc Acid-aldoxime, $Ba(C_4H_3BrNO_3)_2.4H_2O$.—This salt was made by the neutralization of the oxime suspended in water by baric hydrate. It is somewhat sparingly soluble in cold water, more readily in hot water, and may be obtained by the spontaneous evaporation of its aqueous solution in long, glassy, friable needles. The air-dried salt contains four molecules of water, three of which it loses over sulphuric acid, while the fourth cannot be driven off by heat without bringing about decomposition.

I. 0.4350 gram air-dried salt lost over H_2SO_4 0.0388 gram H_2O.

II. 0.8269 gram air-dried salt lost over H_2SO_4 0.0742 gram H_2O.

III. 0.3251 gram air-dried salt gave 0.1270 gram $BaSO_4$.

	Calculated for $Ba(C_4H_3BrNO_3)_2.4H_2O$.	Found. I.	II.	III.
$3H_2O$	9.07	8.96	8.97	....
Ba	23.02	....	....	22.97

0.3317 gram salt dried over H_2SO_4 gave 0.1423 gram $BaSO_4$.

	Calculated for $Ba(C_4H_3BrNO_3)_2.H_2O$.	Found.
Ba	25.32	25.22

Lead Salt of Brommaleïc Acid-aldoxime, $Pb(C_4H_3BrNO_3)_2$.—This salt is sparingly soluble in cold water, and may readily be made from a solution of the sodium salt by precipitation;

when crystallized from boiling water it forms fine, sharp, lustrous needles. The air-dried salt lost nothing over sulphuric acid, and gave the percentage of lead required by the anhydrous salt.

0.3558 gram of the salt gave 0.1811 gram $PbSO_4$.

	Calculated for $Pb(C_4H_3BrNO_3)_2$.	Found.
Pb	34.90	34.77

Silver Salt of Brommaleïc Acid-aldoxime, $AgC_4H_3BrNO_3$. — This silver salt is practically insoluble in water, and was made by the addition of argentic nitrate to a solution of the sodium salt. It is precipitated in white, globular aggregations of microscopic crystals, but it soon darkens, even at ordinary temperatures, and is rapidly blackened on heating. Analyses of the salt well washed with cold water, and dried over sulphuric acid, gave a somewhat too low percentage of silver.

I. 0.3039 gram salt gave 0.1868 gram AgBr.
II. 0.2636 gram salt gave 0.1621 gram AgBr.

	Calculated for $AgC_4H_3BrNO_3$.	Found. I.	Found. II.
Ag	35.88	35.31	35.32

Methyl Ester of Brommaleïc Acid-aldoxime, $C_4H_3BrNO_3.CH_3$. —Unlike the oximes of mucobromic and mucochloric acids, brommaleïc acid-aldoxime is not esterified even by long boiling with methyl alcohol. If, however, a very small percentage of concentrated sulphuric acid is added, the ester is formed without difficulty, and is obtained in colorless needles which melt at 152°–153°. On heating the ester dissolves freely in alcohol, less readily in benzol; it is readily soluble in chloroform, sparingly soluble in ether, and almost insoluble in ligroïn; it may be recrystallized without difficulty from hot water.

I. 0.2168 gram substance gave 0.2263 gram CO_2 and 0.0518 gram H_2O.

II. 0.1460 gram substance gave 0.1317 gram AgBr.

	Calculated for $C_4H_3BrNO_3.CH_3$.	Found. I.	Found. II.
C	28.85	28.45	....
H	2.88	2.65	....
Br	38.46	....	38.39

Brommaleïc Acid-aldoxime Anhydride, $C_4H_2BrNO_2$.—When brommaleïc acid-aldoxime is allowed to stand in the cold with concentrated hydrochloric acid, it gradually dissolves, and large irregular crystals of a new body melting at 78°–80° separate. By extracting the mother-liquors with ether, a small additional amount of the same body may be obtained. The yield is small, and is seriously diminished if the action of the acid is too long continued. While we have observed no similar action with concentrated hydrobromic acid, the new body is formed by the action of concentrated sulphuric acid, and it may most readily be made in this way. The oxime dissolves in a small amount of the concentrated acid, and gives a clear, slightly yellow solution. This solution is then poured into a small volume of cold water, care being taken, with good cooling, to prevent any marked elevation of temperature. The crystals which separate are washed with a little cold water, dried, and recrystallized from carbonic disulphide. The yield in this case was somewhat more than 50 per cent. of the theoretical amount. Analysis showed this body to be the anhydride of the oxime.

I. 0.1900 gram substance prepared with H_2SO_4 gave 0.2047 gram AgBr.

II. 0.1256 gram substance prepared with HCl gave 0.1350 gram AgBr.

	Calculated for $C_4H_2BrNO_2$.	Found.	
		I.	II.
Br	45.45	45.84	45.73

The anhydride, when crystallized from carbonic disulphide, melts at 82°–83°. When cautiously heated between watch-glasses it may be sublimed in delicate needles, which melt at 83°; when heated a few degrees above its melting-point, it gives brommaleïnimide. It dissolves very slowly with apparent decomposition in solutions of the alkaline carbonates. This behavior, together with the melting-point, is sufficient to characterize the substance as the anhydride, and distinguish it from the isomeric imide or cyanide.

Mucochloroxime Anhydride, $C_4HCl_2NO_2$.—It seemed to us advisable to try the action of concentrated hydrochloric and sulphuric acids upon mucochloric acid, the anhydride of which was not obtained by Hill and Cornelison.[1] We followed the methods just described and obtained through the action of each of these acids a body which on analysis proved to be the anhydride.

I. 0.2121 gram substance made with HCl gave 0.3651 gram AgCl.

II. 0.1325 gram substance made with H_2SO_4 gave 0.2289 gram AgCl.

	Calculated for $C_4HCl_2NO_2$.	Found.	
		I.	II.
Cl	42.73	42.55	42.71

Mucochloroxime anhydride crystallizes from carbonic disulphide in irregular aggregations of thick, oblique plates, which melt at 76°–77°. It is readily soluble in alcohol, chloroform or benzol, somewhat sparingly soluble in ether; it dissolves freely in boiling carbonic disulphide, more sparingly in cold; in cold ligroïn it is almost insoluble, but dissolves more freely on heating.

We also made from mucobromoxime, by the action of sulphuric acid, the anhydride melting at 117°–118°, already described.

Brommaleïnimide, $C_4H_2BrNO_2$.—While the oxime of mucobromic and mucochloric acids,[2] like the oximes of the orthoaldehyde-acids[3] of the aromatic series, yield when heated the corresponding imides by isomerization of the anhydrides first formed, we have been unable to prepare brommaleïnimide by heating directly the brommaleïc acid-aldoxime. It already has been said that the oxime melts with explosive decomposition between 140° and 150°, but from the charred product we found it impossible to isolate the imide. By cautiously heating the anhydride, however, a more satisfactory result is obtained, for the imide may then be separated by repeated sublimation from the carbonaceous residue; still only about one-third of the weight of the anhydride taken was obtained. The product agreed with the description of Ciamician and Silber,[4] and melted at 149°–150°.

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[1] This Journal, **16**, 303; Proc. Amer. Acad., **29**, 51.

[2] This Journal, **16**, 299, 304; Proc. Amer. Acad., **29**, 47, 51.

[3] Ber. d. chem. Ges.. **19**, 2278, 2293: **24**, 2346: J. Chem. Soc., **57**, 1069.

[4] Ber. d. chem. Ges., **17**, 557; Kiesielinski: Wien. Acad. Ber., 2 Abth., **74**, 565.

In studying the formation of the oxime anhydride, by the action of sulphuric acid, it was noticed that dichlormaleïnimide and dibrommaleïnimide were formed from the corresponding oximes when the acid was allowed to act at 100°, and Liebermann[1] had already observed, in 1886, that hemipinimide could be made in the same way from the oxime of opianic acid. An attempt to prepare brommaleïnimide by the same method gave negative results.

Products Formed from Brommaleïc Acid-aldoxime by Addition.

The conversion of brommaleïc acid-aldoxime into its anhydride, through the action of sulphuric and hydrochloric acids, has already been described. With hydrobromic acid no formation of anhydride was observed, but instead the products then formed were brommaleïc acid with ammonic bromide, or, on long standing, dibromsuccinic acid. The latter acid was more rapidly formed when the solution of the oxime in glacial acetic acid was saturated with gaseous hydrobromic acid. Precisely the same reaction took place when the oxime was dissolved in glacial acetic acid mixed with 20 per cent. of acetic anhydride, and saturated with gaseous hydrochloric acid (Beckmann's mixture). Ammonic chloride was formed and chlorbromsuccinic acid remained in solution. The residue left on evaporation *in vacuo* over lime, was drained on a porous tile, dissolved in ether and precipitated by the addition of chloroform. The acid thus obtained crystallized in clear, rectangularly truncated prisms, which were quite readily soluble in water or alcohol, more sparingly soluble in ether, and difficultly soluble in chloroform or ligroïn. On heating it remained unaltered up to 170°, and then was gradually decomposed without melting.

I. 0.2072 gram substance gave 0.1596 gram CO_2, and 0.0406 gram H_2O.

II. 0.1017 gram substance gave 0.1447 gram AgCl+AgBr.

	Calculated for $C_4H_4BrClO_4$.	Found. I.	II.
C	20.74	21.01	....
H	1.73	2.18	....
Cl + Br	49.87	....	49.57

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[1] Ber. d. chem. Ges., **19**, 2924.

While we have been unable to prepare addition-products of the oxime itself, either with hydrochloric or with hydrobromic acid, addition-products of the methyl ester can readily be formed from a solution of the oxime in methyl alcohol.

Methyl Ester of Chlorbromsuccinic Acid-aldoxime, $C_4H_4ClBrNO_3.CH_3$.—Brommaleïc acid-aldoxime was dissolved in about five times its weight of methyl alcohol, saturated with gaseous hydrochloric acid. After standing for twenty-four hours the solution was evaporated *in vacuo* over lime, and the residue was washed with ether, dissolved in a little hot alcohol, and filtered from the small amount of ammonic chloride which had been formed through a secondary reaction. The substance left by the alcohol on evaporation was washed with a little cold water, and recrystallized from hot alcohol. Although it is decomposed by long boiling with water, it may also be recrystallized without difficulty from hot water. It crystallized in long, slender, transparent prisms, which melted at 167°–168°. Analysis showed that it had been formed by the addition of hydrochloric acid to the methyl ester of brommaleïc acid-aldoxime.

I. 0.2276 gram substance gave 0.2063 gram CO_2, and 0.0673 gram H_2O.

II. 0.2252 gram substance gave 0.3054 gram AgCl + AgBr and then 0.4339 gram AgI.

III. 0.3597 gram substance gave 18.0 cc. moist nitrogen at 19° and under a pressure of 762 mm.

	Calculated for $C_4H_4ClBrNO_3.CH_3$.	Found. I.	II.	III.
C	24.54	24.71	....	....
H	2.87	3.29	....	....
Br + Cl	47.21	....	47.24	....
Cl	14.50	....	14.80	....
Br	32.71	....	32.25	....
N	5.73	....	....	5.76

Methyl Ester of Dibromsuccinic Acid-aldoxime, $C_4H_4Br_2NO_3.CH_3$.—This substance was formed when a solution of brommaleïc acid-aldoxime in methyl alcohol was saturated with gaseous hydrobromic acid, care being taken to keep the solution cool. On evaporation over lime, a somewhat oily product was obtained, but the liquid portions partially solidified when it was treated with a little cold water. After drying on a porous plate, the substance may be recrystallized from hot alcohol, or it may also be purified by precipitating with ligroïn, its solution in a mixture of alcohol and ether. From alcohol it crystallizes in narrow, flat prisms, which melt at 161°–162°.

0.1553 gram substance gave 0.2033 gram AgBr.

	Calculated for $C_4H_4Br_2NO_3.CH_3$.	Found.
Br	55.37	55.72

Tribromsuccinic Acid-aldoxime, $C_4H_4Br_3NO_3$.—Preliminary experiments showed that brommaleïc acid-aldoxime could be made to unite directly with bromine, but that this addition could not be effected smoothly at ordinary temperatures, and that great care must be taken to exclude all moisture, in order to obtain satisfactory results. The carefully dried oxime was heated for three or four hours at 75° to 80°, with somewhat more than the theoretical amount of bromine, dehydrated with sulphuric acid and diluted with about twenty times its volume of dry chloroform. Under these conditions, the amount of hydrobromic acid formed is small, although its formation cannot wholly be avoided, and the product always contains a little dibrommaleïc acid and ammonic bromide. In this way from 80 to 86 per cent. of the theoretical weight of the addition-product may be obtained. The product is a coarsely crystalline cake, insoluble in the chloroform. It may advantageously be washed with cold and afterward with hot benzol; it is best purified by the precipitation of the ethereal solution with ligroïn. It is then obtained in beautiful rectangular plates, which become opaque and friable with loss of weight soon after they are removed from the mother-liquor. The substance melts with decomposition, accompanied by the evolution of bromine and hydrobromic acid, at a temperature which varies greatly with the rate of heating. When heated at ordinary speed it was found to melt at 133°, but when dipped into a bath heated to 150°, fifteen seconds elapsed before melting.

I. 0.2645 gram substance gave 0.1327 gram CO_2, and 0.0280 gram H_2O.

II. 0.1451 gram substance gave 0.2314 gram AgBr.

III. 0.5064 gram substance gave 18.8 cc. moist nitrogen at 23°.2 and under a pressure of 756 mm.

	Calculated for $C_4H_4Br_3NO_3$.	Found. I.	II.	III.
C	13.56	13.69	....	....
H	1.13	1.18	....	....
Br	67.79	....	67.85	....
N	3.96	....	....	4.16

Dibromacroleïnoxime, $C_3H_3Br_2NO$.—Tribromsuccinic acid-aldoxime, when warmed with water, readily dissolves, but the solution immediately grows turbid with the separation of a more sparingly soluble decomposition-product. If too much water is not used the body separates from the warm solution in fine, felted needles; at the same time carbonic dioxide and hydrobromic acid are formed. For the preparation of this decomposition-product, we have found it advantageous to add the tribromsuccinic acid-aldoxime slowly, with constant stirring, to forty times its weight of water heated to 40°. A part of the product separates at this temperature, and more is obtained as the solution cools. When purified by recrystallization from hot water and dried over sulphuric acid, its percentage composition was found to agree with that of the oxime of dibromacroleïn.

I. 0.3021 gram substance gave 0.1704 gram CO_2 and 0.0372 gram H_2O.

II. 0.1597 gram substance gave 0.2630 gram AgBr.

III. 0.2953 gram substance gave 16.4 cc. moist nitrogen at 20°.2 and under a pressure of 759 mm.

	Calculated for $C_3H_3Br_2NO$.	Found. I.	II.	III.
C	15.72	15.38	....	....
H	1.31	1.37	....	....
Br	69.87	....	70.08	....
N	6.11	....	....	6.34

Dibromacroleïnoxime is readily soluble in alcohol, ether, chloroform, benzol, or carbonic disulphide, but sparingly soluble in ligroïn. It dissolves freely in hot water and almost wholly separates as the solution cools, in slender, tufted needles. When purified by recrystallization from boiling ligroïn, in which, however, it is but sparingly soluble, it melted quite sharply at 104°; but material recrystallized from water, gave a somewhat lower melting-point. It dissolves readily in solutions of the alkaline hydrates, but not in solutions of the alkaline carbonates.

Tribromsuccinic acid-aldoxime is evidently decomposed on heating with water according to the equation,

$$C_4H_4Br_3NO_3 = C_3H_3Br_2NO + CO_2 + HBr.$$

This mode of decomposition is identical with that observed by Petrie[1] in the case of the analogous tribromsuccinic acid.

$$C_4H_3Br_3O_4 = C_3H_2Br_2O_2 + CO_2 + HBr.$$

The yield of crude product, which may be thus obtained from tribromsuccinic acid-aldoxime, amounts to 90 per cent. of the weight calculated according to the above equation.

Dibromacroleïn.—Although the dibromacroleïnoxime may be recrystallized from hot water without difficulty, it is decomposed by prolonged boiling of the solution; the same decomposition is more readily effected by heating with dilute hydrochloric acid; in either case a sharp acroleïn-like odor is developed. In order to identify the products formed, the oxime was heated with dilute hydrochloric acid and the solution distilled with steam until the liquid in the retort was free from odor. This solution was then evaporated to dryness on the water-bath, and the residue washed with ether. Alcohol then dissolved hydroxylamine hydrochlorate, which reduced Fehling's solution in the cold and precipitated brommaleïc acid-aldoxime from a solution of the acid. Whenever crude tribromsuccinic acid-aldoxime was thus boiled with dilute hydrochloric acid, and distilled with steam, dibrommaleïc acid was found in the ethereal washings of the retort-residue, and was identified through the melting-point (114°-115°) of its anhydride, and the character of its barium salt. The aqueous distillate gave the familiar reactions for aldehydes, and with hydroxylamine hydrochlorate it again yielded the dibromacroleïnoxime, melting at 104°. From this solution, however, we were unable to isolate the aldehyde in analyzable form. It could readily be extracted with ether, but, on drying over sulphuric acid, the colorless oil was converted into a viscous, tarry product, which did not invite to farther study. We therefore determined to convert the aldehyde directly into the corresponding dibromacrylic acid, which we thought would present no difficulties in purification and identification. The dilute aqueous solution obtained by distillation with steam was, therefore, warmed with an excess of well-washed argentic oxide. Metallic silver was formed in abundance, together with a soluble silver salt. The residue was thoroughly extracted with hot water, the dissolved silver precipitated with hydrochloric acid, and the filtered solution then extracted with ether. The crude product obtained by the evaporation of the ether closely resembled α-β-dibromacrylic acid, but the yield was very small—not more than 10 to 15 per cent. of the theoretical quantity—the melting-point was low, and the analytical results unsatisfactory. Like α-β-dibromacrylic acid, this acid formed a sparingly soluble acid potassium salt, which crystallized in long, silky needles; the acid, separated from this acid potassium salt, crystallized from ligroïn in stout prisms, which melted at 83°–84°, but we were unable to raise this melting-point by further treatment to the proper point, 85°–86°. The silver salt of the acid formed fine, felted needles, which could be recrystallized unchanged from hot water. A direct comparison of this acid with the α-β-dibromacrylic acid from mucobromic acid,[1] and with the dibromacrylic acid of Fittig and Petri,[2] left no doubt in our minds that we had in our hands the former acid. The small yield and the unexpected difficulties which we met in its purification, made us unwilling to sacrifice the time and material necessary for its more rigorous identification. Evidently the chief importance of further study lay in the fact that tribromsuccinic acid-aldoxime had apparently given a dibromacrylic acid which was isomeric with the acid which may be obtained by a similar reaction from tribromsuccinic acid.

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[1] Ann. Chem. (Liebig), **195**, 70.

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[1] This JOURNAL, **3**, 113; **4**, 169: Proc. Amer. Acad., **16**, 192; **17**, 125.

[2] Ann. Chem. (Liebig), **195**, 70.

Chlormaleïc Acid-aldoxime.

The isolation of a crystalline chlormaleïc acid-aldehyde presents the same difficulties which we met in attempting to prepare the corresponding body containing bromine; the oxime derived from it, however, may easily be made. In order to bring the proper amount of chlorine into reaction, we used the method already described by one of us for the preparation of mucochloric acid.[1] Pyromucic acid was suspended in twenty times its weight of concentrated hydrochloric acid, and the calculated amount (three molecules) of finely powdered manganic dioxide of known strength was slowly added, with careful cooling. After standing for several days, the solution was filtered, diluted, and extracted with ether. On evaporation the ether left a viscous uncrystallizable residue, which was treated with small quantities of cold water, and from this aqueous solution the oxime could easily be obtained by the action of hydroxylamine hydrochlorate. It could hardly be distinguished from the brommaleïc acid-aldoxime, which we have already described. Its behavior toward solvents was also the same, except that it was still more sparingly soluble in ligroïn, and could, therefore, more readily be purified by precipitation with ligroïn from its ethereal solution. When heated in the ordinary way it melted at 150° with decomposition.

I. 0.3165 gram substance gave 0.3711 gram CO_2 and 0.0897 gram H_2O.[2]

II. 0.2009 gram substance gave 0.1943 gram AgCl.

III. 0.3139 gram substance gave 27.2 cc. moist nitrogen at 28° and under a pressure of 760 mm.

	Calculated for $C_4H_4ClNO_3$.	Found. I.	II.	III.
C	32.18	31.98	....	....
H	2.68	3.15	....	....
Cl	23.72	....	23.92	....
N	9.36	....	....	9.51

In order to establish the relation of the oxime to chlormaleïc acid, it was heated with water in a sealed tube for several hours at 110°. The somewhat colored aqueous solution was concentrated, acidified with hydrochloric acid, and extracted with ether. As the acid left by the ether was quite dark colored, it was neutralized with baric hydrate, the barium salt precipitated by alcohol, and the acid again liberated from this purified salt. The colorless acid thus obtained gave the percentage of chlorine required by chlormaleïc acid.

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[1] This JOURNAL, **9**, 160; Proc. Amer. Acad., **22**, 327.

[2] In order to avoid explosive combustion, the substance must be mixed with a large amount of powdered copper oxide.

0.1667 gram substance gave 0.1572 gram AgCl.

	Calculated for $C_4H_3ClO_4$.	Found.
Cl	23.57	23.32

The melting-point of the acid also agreed with the observations of Zincke[1] and van der Riet.[2] In one case the carefully dried acid melted at 106°; another preparation repeatedly recrystallized from water, and dried over sulphuric acid, did not soften below 100°, and melted quite sharply at 111°. Zincke's acid softened at 95° and melted at 106°. Probably the melting-point of chlormaleïc acid, like that of brommaleïc acid, varies with the rate with which it is heated. For the further identification of the acid the barium salt was analyzed.

0.4157 gram of the air-dried salt gave 0.2982 gram $BaSO_4$.

	Calculated for $BaC_4HClO_4.2H_2O$.	Found.
Ba	42.62	42.18

Chlormaleïc Acid-aldoxime Anhydride, $C_4H_2ClNO_2$.—Like the corresponding compound containing bromine, the oxime anhydride can readily be made by the action of concentrated sulphuric acid at ordinary temperatures. The oxime was dissolved in about twice its weight of acid, and the solution slowly poured, with constant shaking and cooling, into cold water. The anhydride at once separates, but as it is somewhat soluble in the diluted acid, the solution may profitably be extracted with ether. The anhydride is readily soluble in the ordinary solvents, except ligroïn. It may conveniently be recrystallized from carbonic disulphide, and forms then brilliant transparent scales which melt at 58°.

0.1814 gram substance gave 0.1978 gram AgCl.

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[1] Ber. d. chem. Ges., **26**, 508.

[2] Ann. Chem. (Liebig), **280**, 227.

	Calculated for $C_4H_2ClNO_2$.	Found.
Cl	26.98	26.97

Methyl Ester of Chlormaleïc Acid-aldoxime, $C_4H_3ClNO_3.CH_3$.—The oxime was dissolved in methyl alcohol, a small percentage of concentrated sulphuric acid added, and the solution boiled with reverse condenser for several hours. The ester crystallized in finely felted needles, which may be recrystallized from hot water or alcohol, and which melt at 130°.

0.1713 gram substance gave 0.1502 gram AgCl.

	Calculated for $C_4H_3ClNO_3.CH_3$.	Found.
Cl	21.69	21.68

Methyl Ester of Dichlorsuccinic Acid-aldoxime, $C_4H_4Cl_2NO_3.CH_3$.—This substance was made by saturating with gaseous hydrochloric acid a carefully cooled solution of the oxime in methyl alcohol. After standing for several days the solution was evaporated *in vacuo* over lime. The semi-solid residue contained ammonic chloride as the product of a secondary reaction; on the addition of water an oil separated which solidified on cooling, but melted again at ordinary temperatures. The oil was, therefore, taken up with ether, the ethereal solution dried with calcic chloride, and again evaporated *in vacuo*; the residue was then freed from oily products by draining on a porous plate. When recrystallized from alcohol, in which it is quite readily soluble, the substance melted at 135°.

0.1058 gram substance gave 0.1511 gram AgCl.

	Calculated for $C_4H_4Cl_2NO_3.CH_3$.	Found.
Cl	35.46	35.31

By the action of gaseous hydrobromic acid upon a solution of the oxime in methyl alcohol can be formed a body which melts at 145°, and which is doubtless the methyl ester of a bromchlorsuccinic acid-aldoxime, isomeric with the body already described, as formed under similar conditions from brommaleïc acid-aldoxime by the action of hydrochloric acid. It has not been further examined.

CII.—ON THE ABSORPTION OF OXYGEN BY TETRABROMFURFURAN.

BY HENRY A. TORREY.

In 1885 Hill and Hartshorn[1] found the α-dibromfurfuran, which they then described, was readily oxidized upon exposure to the air, and they showed that maleïc acid was formed, together with hydrobromic acid, when the oxidation took place in the presence of water. Although tetrabromfurfuran also contains two bromine atoms in the α-position, it may be exposed to the air indefinitely, under ordinary conditions, without essential alteration. The accidental discovery that exposure to direct sunlight quickly brought about a marked change in the physical properties of this body suggested the probability that in this case also the alteration in properties was due to oxidation. At the request of Professor H. B. Hill I made this behavior of tetrabromfurfuran the subject of further study.

Preliminary experiments soon showed that the changes in properties were accompanied by an increase in weight, and that the reaction ran much more rapidly with undiluted oxygen. While the oxidation was more quickly ended at high temperature, the reaction appeared to be more neatly effected at ordinary temperature. The best results were obtained with dry air or oxygen, since the presence of moisture or the vapor of alcohol checked or hindered the reaction. The time required to complete the reaction could materially be diminished by the use of a concave mirror to concentrate the sunlight. Under the most favorable conditions a gain in weight was noted in six or seven hours, which amounted to 80 or 85 per cent. of that required by the addition of one atom of oxygen to each molecule of the tetrabromfurfuran. An examination of the products formed, however, showed that the oxidation was nearly complete, and that the deficit in weight was due to the partial conversion of the dibrommaleyl bromide, which was first formed in the reaction, into dibrommaleïc anhydride. That this conversion was not due to insufficient drying of the oxygen was shown by the fact that sensible quantities of bromine were liberated, if the oxidation was too long continued, and that the presence of free bromine could then be established by the ordinary qualitative tests. The main product of the reaction proved to be the dibrommaleyl bromide, melting at 58°–59°, which was described by Hill and Cornelison.[1] As this body was made by them through the action of bromine upon dibromcrotonolactone, into which it could again be converted by reduction, its structure may be taken to be

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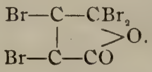
[1] Ber. d. chem. Ges., 18, 448.



$$\begin{array}{lll} \mathrm{Br—C—CBr_2} & & \\ \quad\quad\ | & > \mathrm{O}. & \\ \mathrm{Br—C—CO} & & \end{array}$$

Since the bromine of the dibrommaleyl bromide is directly replaceable by oxygen, its formation from the symmetrical tetrabromfurfuran is also probably due to the displacement of bromine at the outset; the bromine, however, is at first immediately taken up and is thus transferred from one α-carbon to the other without breaking the furfuran ring.

The tetrabromfurfuran used in the course of this work was made by the action of an alcoholic solution of potassic hydrate upon the dibromfurfurantetrabromide described by Hill and Sanger[2] and afterwards further studied by Hill and Hartshorn.[3] It was colorless, well crystallized, and had the proper melting-point, 64°–65°. Since preliminary experiments had shown that complete oxidation could be effected in a much shorter time by the use of undiluted oxygen, no extended experiments were made with air. A weighed quantity of tetrabromfurfuran was introduced into a small, tared flask, which was then connected through sulphuric acid drying-tubes with a gas-holder containing oxygen; a second sulphuric-acid tube passed through the cork of the flask established communication with the atmosphere. After the air contained in the flask had been displaced by dry oxygen, the flask was set in direct sunlight, and the gas-holder so adjusted that the oxygen within the flask was approximately at atmospheric pressure. The tetrabromfurfuran soon turned bright yellow, gradually lost its crystalline structure, and finally became viscous. From time to time the oxygen was driven out by dry air, and the change in weight determined. After six or seven hours of exposure, the maximum, corresponding to from 80 to 85 per cent. of one atom of oxygen, was usually reached, and soon after a loss of weight was observed. The flask was then seen to be filled with the vapor of bromine, which when displaced by dry air, liberated iodine from potassic iodide. Aside from the preliminary tests, five experiments were made with 26.7 grams of tetrabromfurfuran in all. In the first two cases the flask with its contents was heated to 100°; in the remaining three the flask was set upon a white porcelain tile, and the illumination increased by a concave mirror, but no attempt was made to control the temperature. In two out of the three last experiments the liberation of bromine was noticed. In all cases the final product was a reddish-yellow, semi-liquid mass, which solidified completely on standing. On boiling with water the greater part gradually dissolved, and, on distillation with steam, a small amount of unaltered tetrabromfurfuran was usually found in the distillate. The aqueous solution left in the retort contained, beside hydrobromic acid, dibrommaleïc acid. The liquid was neutralized with baric carbonate, the baric dibrommaleate precipitated by alcohol, dried, and finally recrystallized from water. The air-dried salt then contained the proper percentage of barium.

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[1] This JOURNAL, **16**, 207; Proc. Amer. Acad., **29**, 21.

[2] Proc. Amer. Acad., **21**, 145; Ann. Chem. (Liebig), **232**, 55.

[3] Ber. d. chem. Ges., **18**, 449.

I. 0.4246 gram air-dried salt gave 0.2193 gram $BaSO_4$.
II. 0.1902 gram air-dried salt gave 0.0992 gram $BaSO_4$.

	Calculated for $BaC_4Br_2O_4.2H_2O$.	Found. I.	Found. II.
Ba	30.78	30.36	30.66

The free acid was extracted from its aqueous solution by ether, and converted into its anhydride by sublimation. The melting-point of the anhydride was then found to be 113°–114°, while dibrommaleïc anhydride melts at 115°.

Although there could be little doubt that the original oxidation-product contained dibrommaleyl bromide, it seemed advisable to make some attempt to isolate it. On distillation under diminished pressure, the crude product gave a colorless distillate, which passed over at about 140° under a pressure of 25 mm. On cooling in a freezing-mixture, this distillate partially solidified, and by filtration a crystalline substance was obtained, which after recrystallization from ligroïn, melted at 115°. This melting-point and the behavior toward water was sufficient proof that the body was dibrommaleïc anhydride. The liquid filtrate was then mixed with ligroïn, with the hope of separating more of the anhydride, but as it remained clear, the ligroïn was allowed to evaporate spontaneously. On long standing, a few tabular crystals appeared, which, after careful pressing, melted at 58°–59°. Since Hill and Cornelison had found that dibrommaleyl bromide is very slowly attacked by cold water, while dibrommaleïc anhydride is soon converted into the acid, a fresh portion of the crude oxidation-product was finely powdered, and shaken with successive portions of cold water. The aqueous solution contained dibrommaleïc acid, while the insoluble residue could then be recrystallized from ligroïn. Even after repeated recrystallization, the melting-point of the crystalline product could not be raised above 51°–52°, and analysis showed too high a percentage of bromine. On decomposing the body with hot water and distilling with steam, the presence of tetrabromfurfuran could be established, but no means could be found to remove it without decomposing the dibrommaleyl bromide. The presence of the latter body was satisfactorily proved, however, by the formation of dibromcrotonolactone, melting at the proper point (90°–91°), when the substance was reduced with stannous chloride and hydrochloric acid.

Contributions from the Sheffield Laboratory of Yale University.

LIII.—ON HALOGEN ADDITION-PRODUCTS OF THE ANILIDES.

[THIRD PAPER.]

BY H. L. WHEELER, BAYARD BARNES AND J. H. PRATT.

In a recent paper from this laboratory[1] it was shown that the anilides are capable of forming addition-products with bromine and iodine, and that these addition-products can only be formed in the presence of a halogen acid. They are, therefore, perhalides, and it was concluded that these compounds are derivatives of substituted ammonium salts, and that they are perfectly analogous to the perhalides of caesium[2] and ammonium.[3]

We have continued the study of these compounds in order to test the correctness of this view, and also with the object of determining the structure of the halogen salts of the anilides. We have made crystallographic measurements of some of the perhalides and of ammonium triiodide, and we find that, although ammonium triiodide is perfectly analogous to the perhalides of the alkali metals, on the other hand, the perhalides of the anilides, as far as examined, show no crystallographic analogy whatever with these compounds.

This, perhaps somewhat unexpected, result would indicate that the peculiar salts from which the perhalides are derived, are not substituted ammonium compounds, and it will be seen below that other experimental work confirms this conclusion.

All these perhalides are derivatives of two molecules of an anilide with one of a halogen acid, or, briefly, of the 2 : 1 salts. Perhalides derived from 1 : 1 salts have not been prepared. When these salts are employed, the products obtained are invariably derivatives of 2 : 1 salts. However, no special attempt has been made to decide whether the 1 : 1 salts are capable of forming perhalides.

Nölting and Weingärtner[4] were the first to prepare a 2 : 1 salt of the anilides. They found that acetanilide and hydrogen chloride gave a compound represented by the formula $(C_6H_5NHCOCH_3)_2HCl$, and they investigated its behavior on heating. At 250° they obtained ethenyldiphenylamidine, at 280° flavaniline, and at 300° dimethylquinoline. The 1 : 1 hydrochloride of acetanilide was observed by Knorr.[1]

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[1] Wheeler and Walden: This JOURNAL, **18**, 85.

[2] Wells: Am. J. Sci., **43**, 17.

[3] Roozeboom: Ber. d. chem. Ges., **14**, 2398.

[4] Ber. d. chem. Ges., **18**, 1340.

Our work with these salts has shown that the anilides in general form these two series of salts, and no other types have been observed. The anilides differ from their pseudo derivatives, *i. e.*, the imidoesters, both in forming 2 : 1 salts, as well as in not forming 1 : 2 salts. These salts are characteristic for the two series. It is now interesting to note that formanilide gives 2 : 1 salts in the same manner in which the corresponding salts of the other anilides are obtained. The conclusion that follows from this is that formanilide belongs to the series of anilides, and that it has the normal structure.

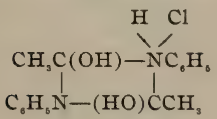
At present there is no occasion to assume that the 1 : 1 salts are anything but substituted ammonium compounds. In the case of the 2 : 1 salts, it is different, and here numerous constitutional formulas are theoretically possible. It will be convenient to discuss these under three heads:

I.—Those which are represented as having the pseudo form of the anilide.

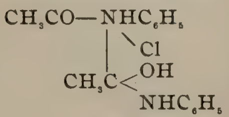
II.—Those in which oxygen or the acyl group takes part in the union of the molecules.

III.—The diammonium structure.

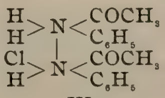
The following formulas are examples of these types:



I.



II.



$$\begin{array}{c} {}^{H}_{H}\!>N<^{COCH_3}_{C_6H_5} \\ | \\ {}^{Cl}_{H}\!>N<^{COCH_3}_{C_6H_5} \end{array}$$

III.

The first type is excluded, since we find that methylmetanitroacetanilide gives perhalides of a 2 : 1 salt, and also since this is an ammonium salt.

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[1] Ann. Chem. (Liebig), **245**, 375.

In regard to the second type, it may be stated that the presence of oxygen, *i. e.*, an acyl group, is unnecessary for the formation of 2 : 1 salts, or of their perhalides. Troost[1] has prepared the compounds $2NH_3.HBr$ and $2NH_3.HI$, and Grimaux[2] has described a perhalide of pyridine represented by the following formula: $(C_5H_5N)_2HBr.Br_4$. Another compound that evidently belongs to this class is the iodine addition-product of benzamide obtained by Curtius:[3]

$$\begin{array}{c} C_6H_5CONH_2.I \\ | \\ C_6H_5CONH_2.I \end{array}$$

On account of these facts, and since the 2 : 1 salts of the anilides are not derived from the pseudo form, the diammonium structure III seems to be most satisfactory. This structure readily allows for the formation of 2 : 1 salts from the secondary anilides, and also explains the lack of analogy of the perhalides to those of ammonium.

A comparison of the perhalides of the anilides with those of the alkali metals, shows other interesting differences besides the lack of analogy in crystalline form.

In this paper we describe mixed perhalides, and show that the hydrochloric acid salts of the anilides readily give perhalides with iodine, while the corresponding perhalides of the alkali metals could not be obtained.

In the case of the bromides and iodine only $CsBrI_2$[4] could be obtained, rubidium and potassium having little or no tendency to form this perhalide. On the other hand, the hydrobromides of the anilides readily unite with iodine. Methylmetanitroacetanilide hydrobromide giving a tetra addition-product.

The relative stability of these perhalides is similar to those of the alkali metals, those containing only iodine being the most stable. Large crystals of the compound $(C_6H_5NHCOCH_3)_2HI.I_2$, after standing in a corked tube for over a year, gave excellent reflections on the goniometer.

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[1] Compt. rend., **92**, 715.

[2] Bull. Soc. Chim. (Paris), **38**, 127.

[3] Ber. d. chem. Ges., **23**, 3040.

[4] Wells: *Loc. cit.*

The property of forming perhalides, and the relatively greater stability of these perhalides, when compared to some of the alkaline metal derivatives, show that it is not basicity that determines their stability or tendency to form, since the salts of the anilides are decomposed by water.

Experimental Part.

Ammonium Triiodide, $NH_4I.I_2$.—This salt was prepared by dissolving the calculated amount of iodine in a strong solution of ammonium iodide and evaporating by standing over potash, as described by Johnson,[1] when dark blue prisms were obtained. These belong to the orthorhombic system and the faces which were observed are as follows :

a, 100. *c*, 001. *d*, 011. *i*, 103.
b, 010. *m*, 110. *e*, 102.

The axial ratio derived from the angles marked with an asterisk in the table below is:

$$a : b : c = 0.6950 : 1 : 1.1415.$$

The crystals are somewhat peculiar in their development, for they show two very similar forms which have no faces alike. They attained a length of 3 mm.

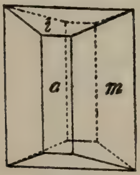

Fig. 1.

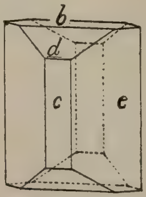

Fig. 2.

Fig. I represents the first form, where the prism *m*, 110 and the dome *i*, 103, are about equally developed, giving the crystals nearly a square outline. The second form of crystals, Fig. II, has nearly the same outline, due to the nearly equal development of the domes *d*, 011 and *e*, 102. The base *c*, 001 has been drawn in front in order to show, to better advantage, the similarity between the two forms. The crystals were generally well developed, but the faces were apt to be dull and somewhat rounded, so that in some cases only approximate measurements could be obtained.

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[1] Ber. d. chem. Ges., **11**, 1268.

The similarity in the crystallization of ammonium triiodide and the alkali metal trihalides, described by Wells, Wheeler and Penfield[1] is very striking, and in the following table the corresponding angles of the alkali triiodides are given for comparison :

		Measured.	NH_4I_3. Calculated.	KI_3.	RbI_3.	CsI_2.
$110 \wedge \bar{1}10$,	$m \wedge m'''$	*69° 36′		70° 34′	68° 53′	68° 37′
$102 \wedge \bar{1}02$,	$e \wedge e'$	*78° 50′			78° 38′	78°
$100 \wedge 011$,	$c \wedge d$	48° 26′–48° 45′	48° 47′		48° 19′	47° 51′
$102 \wedge 011$,	$e \wedge d$	60° 3′	59° 24′			
$103 \wedge \bar{1}03$,	$i \wedge i'$	57° 15′	57° 30′			
c', axis,			1.1415		1.1234	1.1051
a, axis,			0.6950	0.7065	0.6858	0.6824

From the above the ammonium triiodide is shown to be isomorphous with the alkali metal trihalides, while the trihalides of the anilides, as far as examined, show no similarity whatever with the above, the latter crystallizing in either the monoclinic or the triclinic system.

Experiments with Acetanilide.

The 2 : 1 and 1 : 1 *hydrochlorides* of acetanilide[2] separate from an ethyl-acetate or a chloroform solution as a granular precipitate, generally in the form of a mixture, when the solutions are treated with dry hydrogen chloride. The simple salt of the anilides were not obtained in crystals suitable for measurement.

The *Iodhydrochloride*, $(C_6H_5NHCOCH_3)HCl.I_2$.—This salt, as well as the other perhalides described in this paper, was prepared by dissolving the constituents (either the 2 : 1 or 1 : 1 salts and the halogen) in hot glacial acetic acid, and then cooling. The crystals for measurement were generally obtained by slowly evaporating the solution in glacial acetic acid over potassium hydroxide in a desiccator. Better crystals were obtained in this manner than by slowly cooling in a felt box. The crystals in each case were washed free from acetic acid by means of chloroform, and after drying by pressing on paper, were analyzed. The analytical results have been obtained in the gravimetric way ; determination of mixed halogens have been made by igniting the silver salts in a current of chlorine in the usual manner.

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[1] Am. J. Sci. [III], 43, 17 and 478.

[2] *Loc. cit.*

Acetanilide iodhydrochloride, prepared as above, separated in the form of dark-blue, shining needles ; crystals suitable for measurement were not obtained. This and the corresponding salt of parabromacetanilide are the least stable of the perhalides ; they soon lose iodine and turn white.

	Calculated for $C_{16}H_{18}N_2O_2.HCl.I_2$.	Found.
I	45.3	45.9
Cl	6.3	6.6

The 1 : 1 *Hydrobromide*, $C_6H_5NHCOCH_3.HBr$.—This was obtained as a colorless crystalline precipitate. It apparently contained a slight admixture of the 2 : 1 salt.

	Calculated for $C_8H_9NO.HBr$.	Found.
Br	37.0	35.1

The *iodhydrobromide*, $(C_6H_5NHCOCH_3)_2HBr.I_2$, prepared from the above salt, separated in dark-red prisms.

	Calculated for $C_{16}H_{18}N_2O_2.HBr.I_2$.	Found.
I	41.9	41.2
Br	13.2	13.4

The crystallization of acetanilide iodhydrobromide is triclinic, and the following faces have been observed :

c, 001. m, 110. p, $\bar{1}11$.
b, 010. M, $1\bar{1}0$. x, $\bar{4}03$.

The axial ratio derived from the angles marked by the asterisk in the table below was found to be :

$$a : b : c = 0.5707 . 1 : 1.2005 ; \ \alpha = 89° \, 26',$$
$$\beta = 132° \, 20', \ \gamma = 83° \, 16'.$$

The crystals were small, not over 1.5 mm. in length, and were generally doubly terminated. Fig. 3 represents the form of the crystals.

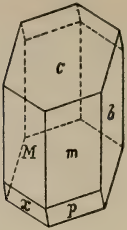

Fig. 3.

The faces were smooth, and gave fair reflections of the signal on the reflecting goniometer. In the table of angles the two extremes of three or more measurements are given.

		Measured.	Calculated.
$c \wedge m$	$001 \wedge 110$	*52° 6′	
$c \wedge b$	$001 \wedge 010$	*83° 2′	
$c \wedge p$	$001 \wedge \bar{1}11$	*66° 3′	
$c \wedge M$	$001 \wedge 1\bar{1}0$	50° 36′–50° 58′	50° 47′
$m \wedge b$	$110 \wedge 010$	74° 50′–74° 55′	74° 55′
$m' \wedge p$	$\bar{1}10 \wedge \bar{1}11$	61° 48′–61° 49′	61° 51′
$b \wedge m$	$0\bar{1}0 \wedge 1\bar{1}0$	*58° 11′	
$m \wedge M$	$110 \wedge 1\bar{1}0$	*46° 54′	

The 2 : 1 *Hydroiodide*, $(C_6H_5NHCOCH_3)_2HI$.—This, and not the 1 : 1 salt, was obtained, both from chloroform and ethyl-acetate solutions of the anilide, on saturating with hydrogen iodide. It is a noticeable fact that hydrogen iodide forms 2 : 1 salts more readily than the other halogen acids.

The *Iodhydroiodide*, $(C_6H_5NHCOCH_3)_2HI.I_2$.—This and the above hydroiodide were described in a previous paper. This perhalide has the greatest tendency to crystallize, some of the crystals being 3 mm. in diameter and 10 mm. in length. They crystallize in the triclinic system, and only three faces were observed which could be determined. These have been taken as the three pinacoids, *c*, 001 ; *b*, 010 ; and *a*, 100. On a few crystals other faces were observed, but they could not be identified.

The inclinations of the axes calculated from the angles of pinacoids, are as follows:

$$\alpha = 102° 56' ; \ \beta = 104° 34' ; \ \gamma = 113° 2'.$$

$a\wedge b$	100∧010	61° 40′
$a\wedge c$	100∧001	67° 47′
$b\wedge c$	010∧001	68° 47′

Experiments with Parabromacetanilide.

The 2 : 1 *Hydrochloride*, $(C_6H_4.Br.NHCOCH_3)_2HCl$.—The formation of 1 : 1 salts in the case of parabromacetanilide was not observed. This compound was obtained as a colorless, crystalline precipitate.

	Calculated for $C_{16}H_{16}N_2O_2Br_2.HCl$.	Found.
Cl	7.6	6.6

The *Iodhydrochloride*, $(C_6H_4Br.NHCOCH_3)_2.HCl.I_2$ was obtained as dark-violet needles.

	Calculated for $C_{16}H_{16}N_2O_2Br_2.HCl.I_2$.	Found.
I	35.3	35.3
Cl	4.9	5.2

The 2 : 1 *Hydrobromide*, $(C_6H_4BrNHCOCH_3)_2HBr$, previously described, gave:

The *Iodhydrobromide*, $(C_6H_4BrNHCOCH_3)_2HBr.I_2$, in the form of red prisms.

	Calculated for $C_{16}H_{16}N_2O_2Br_2HBr.I_2$.	Found.
I	33.2	31.1
Br	10.5	10.6

The 2 : 1 *Hydroiodide*, $(C_6H_4BrNHCOCH_3)_2HI$, was obtained as a colorless, crystalline precipitate.

	Calculated for $C_{16}H_{16}N_2O_2Br_2.HI$.	Found.
I	22.8	22.3

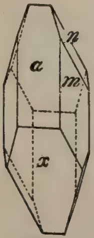

Fig. 4.

The *Iodhydroiodide*, $(C_6H_4BrNHCOCH_3)_2HI.I_2$, prepared from the above, separated in dark-red, triclinic crystals. These attained a diameter of 0.5 mm. The faces observed are the following :

a, 100 ; *m*, 110 ; *x*, $\bar{1}01$; *n*, 011.

The faces were smooth and bright and gave good reflections. From the angles marked by an asterisk in the table below, the following axial ratio was determined :

$$a : b : c = 1.853 : 1 : 3.015 ; \ \beta = 79° \tfrac{1}{2}'.$$

		Measured.	Calculated.
$a' \wedge n$	$\bar{1}00 \wedge 011$	*93° 30′	
$m \wedge n'$	$110 \wedge 0\bar{1}1$	*142° 40′	
$a \wedge m$	$\bar{1}00 \wedge 110$	*61° 31′	
$a' \wedge x$	$\bar{1}00 \wedge \bar{1}01$	34° 28′	34° 24′
$m''' \wedge d'$	$\bar{1}10 \wedge 0\bar{1}1$	30° 28′	30° 43′
$d \wedge x$	$011 \wedge \bar{1}01$	82° 47′	82° 45½′
$m' \wedge x$	$\bar{1}10 \wedge \bar{1}01$	66° 35′	66° 35½′
$m'' \wedge d'$	$\bar{1}\bar{1}0 \wedge 0\bar{1}1$	36° 44′	36° 46′

The *Iodhydroiodide*, $(C_6H_4BrNHCOCH_3)_2HI.I_4$, was obtained in the form of deep-red, monoclinic twins. Enough faces were not shown to permit of satisfactory crystallographic description.

	Calculated for $C_{16}H_{16}N_2O_2Br_2HI.I_4$.	Found.
I	59.68	59.75

Experiments with Methylmetanitroacetanilide.

The 1 : 1 *Hydrobromide*, $C_6H_4NO_2NCH_3COCH_3.HBr$.—This and not the 2 : 1 salt was obtained directly in the form of a colorless, crystalline precipitate.

	Calculated for $C_9H_{10}N_2O_3.HBr$.	Found.
Br	29.0	28.3

The *Bromhydrobromide*, $(C_6H_4NO_2NCH_3COCH_3)_2HBr.Br_2$.—The above 1 : 1 salt gave this perhalide in the form of small dark-yellow, well-developed, stout prisms. It slowly evolves bromine on exposure.

	Calculated for $C_{18}H_{20}N_4O_6HBr.Br_2$.	Found. I.	Found. II.
Br	38.1	37.2	37.4

The *Iodhydrobromide*, $(C_6H_4NO_2NCH_3COCH_3)_2HBr.I_4$.—This was obtained as a black mass, which under the microscope appeared to consist of needles. The powder was dark bottle-green.

	Calculated for $C_{18}H_{20}N_4O_6HBr.I_4$.	Found.
Br	8.1	8.1
I	51.9	52.8

When hydrogen iodide was passed into an ethyl acetate solution of methylmetanitroacetanilide, the acid was reduced and no precipitate was formed.

Experiments with Formanilide.

The 2 : 1 *Hydrochloride*, $(C_6H_5NHCHO)_2HCl$.—When hydrochloric acid is passed into a solution of formanilide in dry benzene, the product obtained is generally a mixture of the 2 : 1 and 1 : 1 salts. The 2 : 1 salt was obtained as a colorless, crystalline precipitate, which soon absorbed moisture and decomposed on exposure.

	Calculated for $C_{14}H_{14}N_2O_2.HCl$.	Found.
Cl	12.7	12.3

The 2 : 1 *Hydroiodide*, $(C_6H_5NHCHO)_2HI$.—The salt, obtained apparently in the form of needles from a benzene solution, rapidly absorbs moisture from the air, becoming sticky and decomposing. For analysis it was rapidly pressed on paper and dried over sulphuric acid in a vacuum-desiccator. The analysis indicates that a slight decomposition was not avoided :

	Calculated for $C_{14}H_{14}N_2O_2HI$.	Found.
I	34.3	31.2

The 1 : 1 *Hydroiodide*, $C_6H_5NHCHO.HI$, differs decidedly in appearance from the above 2 : 1 salt. It separates from an ethyl-acetate solution in granular condition, and is more stable. An iodine determination gave 48.0 per cent. of the halogen instead of the 51.0 per cent.

Attempts were made to prepare perhalides from the salts of formanilide, but when these were warmed in glacial acetic acid the anilide was saponified. Similar results were obtained with the salts of paraformtoluide, the salts of the formyl compounds being considerably less stable than those containing the acetyl group.

Other Experiments.

The 2 : 1 *Hydrochloride*, $(C_6H_4NO_2NHCOCH_3)_2HCl$, was obtained from a chloroform-solution of metanitroacetanilide and hydrogen chloride.

	Calculated for $C_{16}H_{16}N_4O_6.HCl$.	Found.
Cl	8.9	8.7

Under similar conditions methylacetanilide, diphenylbenzamide, diethylbenzamide, and methylbenzanilide gave no precipitate with either hydrogen chloride or bromide, ethyl acetate or chloroform being used as the solvent. Benzamide was not precipitated from a chloroform solution by hydrogen chloride, although this amide gives salts with the halogen acids. From ethyl acetate hydrogen chloride and bromide precipitated the 1 : 1 salts of paraformtoluide, and from benzene, benzamide was precipitated as a 1 : 1 salt by hydrogen iodide.

NEW HAVEN, May, 1897.

ON THE PERMEATION OF HOT PLATINUM BY GASES.

BY WYATT W. RANDALL.

In connection with a research which has been in progress for some time, and in which the attempt is being made to prepare absolutely pure hydrogen for spectroscopic examination, the author has endeavored to free the gas from impurities by filtering it through a diaphragm of hot platinum. The spectroscopic results obtained will be published later; it seemed worth while, however, to give at this time a short account of the work which has been done in the past in the matter of the permeation of metals by hydrogen, and also of the measure of success which has attended the attempt to free the gas from impurities by the method mentioned.

The fact of the permeability of hot platinum by hydrogen was first announced by Deville and Troost.[1] When hydrogen was introduced into a hot platinum tube surrounded by one of porcelain filled with air, the former gas passed through the walls of the metal tube, but no passage of air into the inner tube could be detected. Later papers by the same authors[1] established the results claimed and showed that iron also was permeable by certain gases at high temperatures.

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[1] Compt. rend., **56**, 977, (1863); Phil. Mag., [4], **26**, 336; Abstr.. Jsb., 1863, 23; Chem. News, **7**, 294.

A year or two later Graham[2] repeated the experiments of Deville and Troost, taking, however, greater precautions to avoid error. His method differed in that, by means of a Sprengel pump, a vacuum was maintained within a platinum tube, which was closed at one end, and which was heated in an atmosphere of hydrogen. The gas was found to penetrate rapidly into the interior of the tube. When air was substituted for hydrogen, practically no gas was delivered by the pump, but Graham was of the opinion that air did penetrate to a slight extent. As however the connections of his apparatus were not above suspicion, and as he employed air which had been dried by sulphuric acid alone, the evidence for the penetration by air is by no means convincing. At the temperature employed, any water-vapor present in the air would probably have been at least partially dissociated and free hydrogen have been formed. The same objection might hold good for all his experiments in this series. When carbon dioxide was tried, 0.3 cc of gas was collected by the pump and "an indeterminate small portion of this was condensed by baryta water and appeared to be carbonic acid." In view of the power of carbon dioxide to cling to the walls of a vacuous glass tube and to be but slowly removed, the evidence here, again, is inconclusive. Negative results were obtained with chlorine, hydrochloric acid gas, steam, and ammonia. When coal-gas containing hydrogen, methane, carbon monoxide and ethylene, was employed, hydrogen penetrated, but no evidence of carbon compounds could be obtained on exploding the gas collected with oxygen. Graham concluded that a little nitrogen might penetrate the platinum wall provided hydrogen was passing through at the same time in the opposite direction, since he obtained evidence of such penetration when the tube was filled with hydrogen and heated in an atmosphere of nitrogen.

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[1] (*a*) Compt. rend., **57**, 894, (1863); (*b*) *Ibid.*, **57**, 965; also Ann. Chem., (Liebig), **130**, 254; (*c*) Compt. rend., **59**, 102, (1864); Abstr. Jsb., 1864, 89; Phil. Mag., [4], **28**, 229; Chem. News, **10**, 57.

[2] Phil. Trans., **156**, 399. (1866); Phil. Mag., [4], **32**, 503; J. Chem. Soc., **20**, 257; Abstr. Proc. Roy. Soc., **15**, 223.

In accordance with conclusions arrived at by a study of the passage of gases through various septa, Graham assumed that the penetration of platinum by hydrogen was due to the liquefaction of the gas on the surface, the diffusion of the condensed gas through the material of the wall, and the evaporation of the liquid from the inner surface of the tube into the vacuum.

Nearly all research in this field since the publication of these results has had to do with the nature of the occluded gases, and not with questions of penetration considered by itself. Morse and Burton, however, have shown[1] that the hydrogen contained in the flame of an ordinary blast-lamp will penetrate a platinum vessel heated by that means; and Ramsay, in studying the phenomena connected with the passage of hydrogen through a palladium septum, has found[2] that this power was apparently possessed by no other gas examined. As palladium is permeable to a far higher degree than platinum, it would naturally be assumed that the latter metal would resist the passage of all gases except hydrogen completely.

In his studies of the properties possessed by hydrogen when occluded in platinum and palladium, Graham found that the metals could be more highly charged with the gas by making them serve as the negative pole of galvanic cells, than by heating them and allowing them to cool in an atmosphere of hydrogen.[3] "The occluded hydrogen," he says, "is certainly no longer a gas, whatever may be thought of its physical condition." Oxygen was not occluded when the current was reversed. The evidence, he considered, was on the whole against the view that chemical combination takes place between the metal and the gas. Careful examination of the change in volume suffered by palladium and its alloys on absorbing hydrogen led to the view that the gas was converted into a metal-like substance and formed a species of alloy with the palladium.[1] Hydrogen in this particular condition—"Hydrogenium," as Graham calls it—is magnetic, shows electric conductivity and possesses some tenacity. Its density varies: in palladium alloys it is 0.711–0.7545; in palladium itself, 0.854–0.872.

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[1] This JOURNAL, **10**, 148, (1888). It is to Professor Morse that I owe the suggestion of employing a platinum septum in this work.—W. W. R.

[2] Phil. Mag. [5]. **38**, 206, (1894).

[3] Proc. Roy. Soc., **16**, 422, (1868).

This conclusion was, however, challenged in the more recent work of Berthelot,[2] who as a result of thermochemical investigations, returned to the view that definite complex hydrides of palladium and platinum are formed. The results obtained by Thoma[3] had to do with the absorption of the gas considered as a case of solution capable of supersaturation. The conclusions of Berthelot have been offset by a research by Mond, Ramsay and Shields[4] upon platinum-black, in which doubt was cast upon the purity of the material used by the French chemist, and evidence given to show the untrustworthiness of his thermochemical data for establishing the condition of the occluded gas.

The method of spectroscopic examination seemed capable of yielding so much more accurate results in determining the presence of foreign gases in the filtered hydrogen than any of the analytical methods to my knowledge used hitherto in this work, that it seemed worth while to put it to trial. Tubes filled with gas were examined in the Physical Laboratory of this University, with the aid of a large concave grating specially prepared for such work, and photographs were made of each in turn. For their kindness in making these examinations, I am indebted to Dr. J. S. Ames and Mr. W. J. Humphreys.

The essential features of the apparatus used in the production of the gas to be tested are represented in the accompanying figure. It consists of a platinum tube, *AA'*, about 350 mm. long, and of about 3 mm. internal diameter, closed at one end and sealed at the other, by means of fusible glass, into a soft-glass tube, which is in turn connected with the sparking-tube *D* and the Töpler pump. The closed end of

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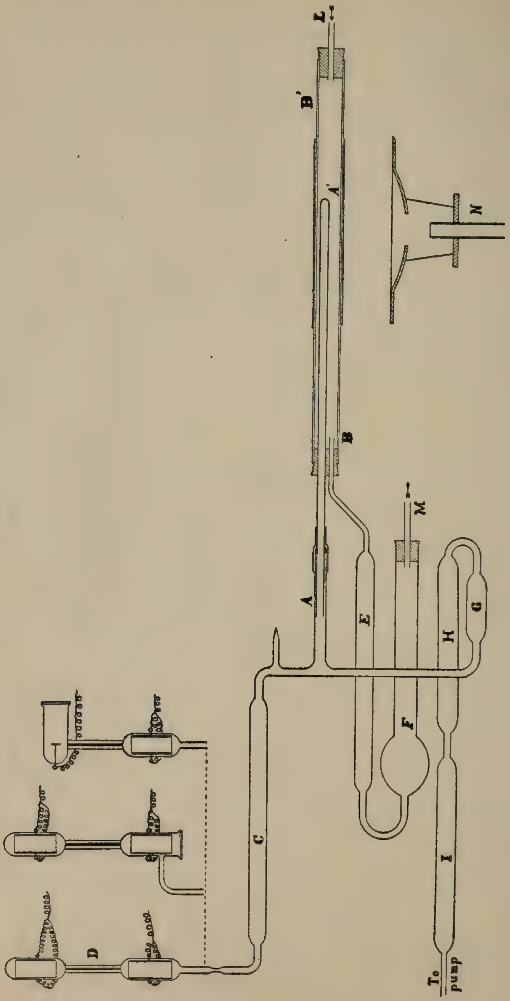
[1] Proc. Roy. Soc., **17**, 212, 500, (1869): Compt. rend., **68**, 1511.

[2] Compt. rend., **94**, 1377. (1882); Ann. chim. phys., [5], **30**, 519.

[3] Ztschr. phys. chem., **3**, 69, (1889).

[4] Phil. Trans., 186 A, 657, (1895); Abstr. Proc. Roy. Soc., **58**, 242.


L
B'
A'
N
B
M
A
E
H
G
C
F
I
D
To pump

the platinum tube projects into a piece of hard-glass tubing, *BB'*, through which a current of dry gas, entering at *L*, could be passed, while at the same time the platinum tube can be heated by means of a Bunsen burner, *N*, below the combustion-tube. The latter is covered for a portion of its length with a layer of thick copper foil to distribute the heat, and with the aid of asbestos-board screens the temperature of the two tubes can be raised to a white heat. A plug of asbestos was pushed into the annular space between the two tubes to give support. A short piece of black rubber is drawn over the place where the platinum tube is sealed into the glass tube, is wired on and well shellaced, to guard against possible leakage from fracture.

The tube *C* is filled with phosphorus pentoxide. The gas entering at *L* has been made to pass through sulphuric acid, calcium chloride, soda-lime, and, finally, through a long tube filled with phosphorus pentoxide. It passes out at *B* through the guard-tubes *E* containing the pentoxide, and *F* containing calcium chloride and soda-lime. When hydrogen was the gas employed, it was first passed through four wash-bottles filled with acid, and two filled with alkaline permanganate solution, and then through a tube filled with red-hot copper turnings, on its way to the drying-tubes. It was hoped the latter device would free the gas from any admixture of oxygen, whether present as a constituent of air, or given off from the permanganate solution.[1]

The sparking-tubes were of several forms, at first with wire electrodes, afterwards with cylindrical electrodes of aluminium tubing or foil. In some cases photographs were made of the spectrum of the light emitted through the walls of the capillary tube ; in others, of that observed " end on " through a disk of quartz sealed as a window to one of the bulbs. In one case the tube was specially constructed so that the light observed through the window was that produced at the electrode and not that in the capillary tube ; the light thus obtained was, however, so weak that no photograph could be made of the spectrum.

Having demonstrated the tightness of the apparatus and the fact that at the temperature employed hydrogen is capable of permeating the walls of the platinum tube, experiments were made which afforded evidence that a similar power of penetration is not possessed by oxygen or nitrogen. Air was drawn through the apparatus while the metal tube was maintained at a white heat. Care was of course taken to have the air as dry as possible in order to avoid the presence of hydrogen through the dissociation of water-vapor. The vacuum within the metal tube could be maintained apparently indefinitely under these conditions.

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[1] See note 1, p. 691.

The tubes were filled with hydrogen as follows: The carefully cleansed tube was sealed to the apparatus and, when the air had been completely exhausted, was left for twenty-four hours or more; by this time all moisture was probably removed by the phosphorus pentoxide. By continuous sparking and exhaustion the gas occluded by the electrodes was then removed, and a condition of brilliant green fluorescence readily obtained. On raising the mercury in the Töpler pump so as to compress all the gas in its bulb and tubes into a space of not more than a fraction of a cubic centimeter, and at the same time noting the change, if any, which took place in the height of the mercury column in the delivery-tube—in other words, on using the pump itself as a McLeod gauge—it could be shown that the pressure within the exhausted space was not more than one or two millionths of an atmosphere. Connection between the pump and the rest of the apparatus was then cut off by turning a glass tap, and hydrogen was admitted slowly into the sparking-tube by heating the metal tube while a current of dry purified gas was circulating about it. When the pressure inside the sparking-tube had reached about 1 cm., the heating was discontinued and the apparatus exhausted as before. The process of filling and exhausting was repeated from three to six times, after which the tube was filled to the desired pressure—which was between 3 and 8 mm.—and was sealed off. In some cases, as an extra precaution, the tube was enclosed in a copper air-bath and heated during the process of exhaustion to a temperature of 150°–200°, the sparking being meantime continued.

It may be as well to say that the passage of the hydrogen into the exhausted space was very slow as compared with what the statements of Graham had led me to expect. It may be that the tube employed by me was thicker and more thoroughly hammered, and that the temperature obtained was not so high. At all events the pressure in the sparking-tube rose only at the rate of about a millimeter in three to five minutes, the volume of all the tubes and connections open to the gas being about 100 cc. On this account the time required to cleanse, exhaust, and fill the tube in the manner described, waiting in each case for diffusion to equalize the pressure throughout the long system of tubes, rendered the work very slow and tedious, especially as only a short time was available on any one day to be devoted to the work.

The sparking-tubes had at first, except for the tube *C*, been in direct connection with the Töpler pump and mercury gauges. On photographing the spectrum it was found that the gas was contaminated with the vapor of mercury. To avoid this difficulty the tubes *G*, *H*, and *I* were introduced between the pump and gauges and the system to be exhausted. *I* is a long tube filled with powdered sulphur, *H* a similar one containing bright copper turnings, and *G* contains gold-leaf. *H* and *I* are shown in the figure much shorter in proportion than they are in reality. So perfectly do these guard-tubes serve their purpose, that after one year the gold-leaf shows no signs of amalgamation. The copper has apparently held back all sulphur-vapors from the sparking-tubes, whereas the mercury in the manometers have become fouled from not being protected in its turn by copper. No trace of mercury-vapor has been detected in the gas contained in any of the sparking-tubes since the precautions mentioned were taken to exclude it.

Results.

A careful examination of the photographic negatives obtained when the hydrogen produced as described and contained in the sparking-tubes was used as the source of light, has failed to reveal the presence of any other substance—unless the so-called "compound" spectrum is to be considered an indication of such contamination. The purified hydrogen drawn through the combustion-tube *BB′* probably frequently contained nitrogen, but no signs of that gas could be detected in the spectrum of what had passed into the inner tube. If the compound spectrum is due to the presence of water-vapor, it is not clear how it can be eliminated, no more efficacious drying agent than phosphorus pentoxide being available.

It may be well to mention here that the results obtained in the examination of the spectrum of hydrogen purified as described in this paper, do not seem to agree with those obtained by Messrs. Trowbridge and Richards.[1] According to these authors an oscillatory discharge from their powerful storage-battery through hydrogen did not yield the compound spectrum, whereas the direct discharge produced the compound spectrum as usual. In the experiments performed with hydrogen, as described in this paper, the discharge was that of a large Ruhmkorff coil, sometimes with and sometimes without a Leyden jar in the secondary circuit and with considerable variations of current in the primary coil. In no case was the compound spectrum absent. Messrs. Trowbridge and Richards do not mention the character of the tubes they employed, nor give any account of the method of purification used for the gas or that of cleansing and filling the tubes. It is just possible that were these data available, some explanation of the difference in our results might be forthcoming. It is true that the pressures used in this work were on the average a little higher than those employed by Trowbridge and Richards, but not to an extent, in all probability, sufficient to account for so marked a discrepancy.

As has been stated, oxygen and nitrogen do not penetrate hot platinum under the conditions described above; it remained an interesting question to determine whether this was due in any degree to the relatively high specific gravity of these gases as compared with hydrogen. Accordingly an experiment was made to see if marsh-gas, with a density only half that of oxygen, would penetrate into the inner tube. A large gasometer was filled with the gas prepared by heating a mixture of dehydrated sodium acetate and soda-lime, and washed with water and acid sodium sulphite solution to remove the vapors of acetone. After standing several weeks in contact with water in the gasometer, it was passed again through a solution of the sulphite, through soda-lime, calcium chloride, and sulphuric acid, to mix with the purified hydrogen as it entered the tube filled with hot copper turnings mentioned above.[1] After the air had been removed, and a gas-mixture, consisting of about four-fifths marsh-gas and one-fifth hydrogen, was being passed through the combustion-tube *BB'*, the latter was heated. Gas passed very slowly into the sparking-tube; after about three hours the pressure had risen to only about 3 mm. Examination of the gas, by means of a large prism spectroscope, failed to show the presence of any carbon compound; but, on account of the low pressure, the light was too feeble to give any result with the photographic method, even after a very long exposure, and so this experiment will still require further and more accurate confirmation.

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[1] Am. J. Sci., [4], **3**, 118; Phil. Mag., [5], **43**, 137, (1897).

It is proposed to continue this work with hydrogen and other gases.

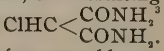
Since this paper was written, a note has been published by Ramsay and Travers,[2] in which they describe their attempts to pass helium and argon through septa of platinum, palladium, and iron, under conditions similar to those described in this paper. No evidence of such penetration was however obtained.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY, June, 1897.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON SOME MALONIC ACID DERIVATIVES.

BY RICHARD S. CURTISS.

In their researches upon the haloid derivatives of ethyl malonate, Conrad and his students found that when ethyl chlormalonate was treated with cold concentrated alcoholic ammonia, the chlorine atom remained intact, the resulting crystalline compound being chlormalonamide,  $ClHC<\begin{matrix}CONH_2\\CONH_2\end{matrix}$.[3] When, however, the reaction was continued for several hours at 140° in a sealed tube, a small yield of a compound was obtained,[1] apparently imidodimalonamide, $NH<\begin{matrix}CH<\begin{matrix}CONH_2\\CONH_2\end{matrix}\\CH<\begin{matrix}CONH_2\\CONH_2\end{matrix}\end{matrix}$ along with some amidomalonamide, $NH_2—CH<\begin{matrix}CONH_2\\CONH_2\end{matrix}$.

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[1] It is not generally known that comparatively large quantities of oxygen are set free when hydrogen is made to bubble through potassium permanganate solution. Unless care is taken to remove this oxygen, say with red-hot copper and a drying agent, an opportunity is given for a very serious error in all experiments where pure hydrogen is desired. This reduction of permanganate by hydrogen is now under investigation in this laboratory by Prof. Morse.—W. W. R.

[2] Chem. News, **75**, 253.

[3] Conrad and Bischoff: Ann. Chem. (Liebig), **209**, 231

Ethyl chlormalonate, heated with boiling aniline for ten hours, gave a crystalline anilidomalonanilide,

$$C_6H_5NH—CH<\begin{matrix}CONHC_6H_5\\CONHC_6H_5\end{matrix}.$$

Conrad and Brückner[2] obtained by the action of concentrated alcoholic solution of ammonia on ethyl dichlormalonate, at ordinary temperatures, dichlormalonamide, $Cl_2C<\begin{matrix}CONH_2\\CONH_2\end{matrix}$, and dichloracetamide, while ethyl dibrommalonate treated with cold alcoholic ammonia, gave a small yield of an unstable body, doubtless, from the analysis, diamidomalonamide, and also some dibromacetamide. This diamidomalonamide, heated to 90°–100°, readily loses ammonia and gives a small amount of a substance which appears to be imidomalonamide, $NH=C<\begin{matrix}CONH_2\\CONH_2\end{matrix}$.

In these experiments the ester seems to be converted into the amide before the haloid is substituted. On treating ethyl brommalonate with aniline, a weaker base than ammonia, one might expect an easy substitution of the bromine, without affecting the carbethoxyl group, with the formation of ethyl anilidomalonate, $C_6H_5NH—CH<\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix}$. Wishing to obtain this body and a knowledge of its properties for use in further research, this reaction has been carried out with satisfactory results.

The oxidation by mercuric oxide of ethyl anilidomalonate has led to the unexpected formation of ethyl dianilidomalonate, $\begin{matrix}C_6H_5NH\\C_6H_5NH\end{matrix}>C<\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix}$. I have also made this substance by the action of aniline on ethyl dibrommalonate, and have studied its properties.

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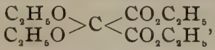
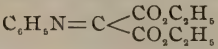
[1] Conrad and Guthzeit: Ber. d. chem. Ges., **15**, 605.

[2] *Ibid.*, **24**, 2994.

I have further investigated the behavior of sodium ethylate on ethyl dibrommalonate, with the view of forming ethyl diethoxymalonate,  $\begin{matrix}C_2H_5O\\C_2H_5O\end{matrix}>C<\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix}$, which, it was thought, would possibly lose alcohol on being treated with aniline and give ethyl phenylimidomalonate,  $C_6H_5N=C<\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix}$, by analogy with the behavior of the ketone ortho ethers toward aniline.[1]

Since the completion of my work in this line, a paper has appeared by Bischoff,[2] in which he announces the discovery of ethyl diethoxymalonate. I shall include the results of this part of my work, however, as they confirm his experiments and have been carried out somewhat more fully and under slightly different conditions.

The Action of Aniline upon Ethyl Brommalonate.

The ethyl brommalonate was prepared according to the method of Knoevenagel,[3] and the fraction boiling at 120°–122° under 14 mm. pressure, was used in the experiments. 49 grams of ethyl brommalonate were mixed with 56 grams (3 molecules) of aniline, and the mixture allowed to stand at ordinary temperatures. At first there was a slight evolution of heat. Aniline hydrobromide crystals soon formed, and in two hours the reaction was almost complete. After standing four days, the liquid was filtered off from the crystals, which weighed, after being washed with ether and dried, 32 grams (93 per cent. of the theoretical yield). The excess of aniline was removed from the ether solution of the filtrate by dilute hydrochloric acid, the ether dried over fused potassium carbonate and evaporated in a vacuum. The crystals which formed, washed with ligroïn, weighed 31 grams, and proved to be ethyl anilidomalonate. From the mother-liquor a small amount of the same body was obtained, together with a small amount of needle-like crystals, which melted at 117°–118°, and were ethyl dianilidomalonate, formed undoubtedly from a small amount of ethyl dibrommalonate, which it was impossible thoroughly to separate from the monobrom derivative by fractional distillation.

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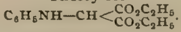
[1] Claissen: Ber. d. chem. Ges., **29**, 2932.
[2] *Ibid.*, **30**, 487; **29**, 1507.
[3] *Ibid.*, **21**, 1356.

The chief product was recrystallized from alcohol, dried in a vacuum over sulphuric acid, and on analysis:

0.2977 gram of the substance gave 0.6745 gram CO_2, and 0.1899 gram H_2O.

0.2820 gram of the substance gave 14.8 cc. N at 17°, and 746.8 mm.

	Theory for  $C_6H_5NH—CH<\begin{smallmatrix}CO_2C_2H_5\\CO_2C_2H_5\end{smallmatrix}$.	Found.
C	62.15	61.80
H	6.77	7.08
N	5.58	6.00

Ethyl anilidomalonate crystallizes from alcohol or ligroïn in crystals 2 cm. or more long, which belong to the monoclinic system; it has a greenish-white tint, a bitter taste, melts at 44°–45° to a clear liquid, is easily soluble in carbon disulphide, alcohol, ether, benzene, and chloroform; fairly soluble in ligroïn (boiling-point 70°–80°), insoluble in water and dilute hydrochloric acid, and soluble in potassium hydrate solution. It decomposes on heating, turns dark, and gives off an odor similar to that of an isonitrile. Dry hydrochloric acid gas gives, in an ethereal solution of the body, a colorless crystalline compound, soluble in much ether. In alcoholic solution with alcoholic sodium ethylate, at ordinary temperatures, a sodium salt is precipitated. One molecule of bromine in a chloroform solution of the ester gives fine silky white needles with little loss of hydrobromic acid.

Pure ethyl anilidomalonate reduces an ammoniacal silver nitrate solution very strongly, even in the cold, and is easily oxidized by mercuric oxide when heated.

Oxidation of Ethyl Anilidomalonate by Mercuric Oxide.

Six grams of ethyl anilidomalonate in 10 cc. of ligroïn (boiling-point 100°–110°), together with 8 grams of freshly precipitated dry mercuric oxide, were heated for three hours at 95°–100°, in a flask with a reverse condenser. Much metallic mercury separated out. The liquid, filtered from the mercury salt and evaporated in a vacuum, gave five grams of a green oil, from which 2.5 grams of a crystal compound were obtained. This, purified by boiling in alcoholic solution with bone-charcoal and recrystallized from alcohol, gave rosettes of white, silky needles, melting at 117°–118°. On analysis this body proved to be ethyl dianilidomalonate instead of the expected ethyl phenylimidomalonate. The study of this peculiar reaction will therefore be continued.

0.2735 gram substance gave 0.6652 gram CO_2, and 0.1596 gram H_2O.

	Theory for $(C_6H_5NH)_2>C<(CO_2C_2H_5)_2$.	Found.
C	66.66	66.33
H	6.43	6.48
N	8.19	....

The Action of Aniline upon Ethyl Dibrommalonate.

The ethyl dibrommalonate was made according to the method of Conrad and Brückner,[1] and the fraction boiling at 142°–143°, under 18 mm. pressure, was used in these experiments.

19 grams of the ethyl dibrommalonate were mixed with 28 grams of aniline (5 molecules). There was no perceptible evolution of heat, but aniline hydrobromide soon began to separate out. After allowing the mixture to stand at 50°–60° for six days, it was extracted with ether, leaving 18 grams of aniline hydrobromide, or 85 per cent. of the theoretical yield. The ethereal filtrate evaporated on the water-bath gave 10.5 grams of impure crystals which, after filtering on the pump, are best freed from the adhering oil by spreading on a clay plate.

Purified by recrystallizing from 60 per cent. alcohol, after boiling with bone-charcoal, the body melts at 117°–118°, and distils with little decomposition. It crystallizes from absolute alcohol in rosettes of long, colorless, silky needles, easily electrified by rubbing. It is easily soluble in ether, acetone, aniline, carbon tetrachloride, and acetic ether; fairly so in alcohol, and difficultly soluble in ligroïn. It dissolves in concentrated hydrochloric acid, is not readily saponified by aqueous potash; but sodium alcoholate gives an immediate precipitate of sodium salt from an alcohol solution.

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[1] Ber. d. chem. Ges., **24**, 3001.

Purified as above, dried in a vacuum over sulphuric acid and analyzed, it gives the following results:

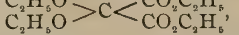
0.2345 gram of the substance gave 0.5730 gram CO_2, and 0.1380 gram H_2O.

0.2347 gram of the substance gave 17.2 cc. N at 23°, and 733.5 mm.

	Theory for $(C_6H_5NH)_2>C<(CO_2C_2H_5)_2$.	Found.
C	66.66	66.64
H	6.43	6.54
N	8.19	7.97

This body is not oxidized by mercuric oxide or ammoniacal silver nitrate solution, and is identical in every respect with the product obtained by the oxidation of ethyl anilidomalonate described above. It can be heated for an hour in sealed tubes at 100°–120°, with little apparent change. Heating with aniline at temperatures ranging from 100°–200°, in sealed tubes, with the idea of forming dianilidomalonanilide, gave no satisfactory results.

The Action of Sodium Ethylate on Ethyl Dibrommalonate.

The interaction between ethyl dibrommalonate and alcoholic sodium ethylate under various conditions, such as temperature; an excess of one or the other reagent; mode of mixing was found to give in all cases a complicated mixture of compounds. Ethyl diethoxymalonate,  $\begin{matrix}C_2H_5O\\C_2H_5O\end{matrix}>C<\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix}$, which it was expected would be the chief product of the reaction, was obtained in largest amount when the following conditions were present: 95.8 grams of ethyl dibrommalonate in 30 cc. of absolute alcohol were dropped, by means of a separating funnel, into 225 cc. of absolute alcohol, in which 13.8 grams (2 atoms) of sodium had been dissolved. The temperature was kept at 48°–50° by the heat of the reaction, and a small amount of carbon dioxide gas was continuously evolved. When all the ethyl dibrommalonate had been added the mixture was allowed to stand for one hour at 60°. The contents of the flask then consisted of a large amount of light-colored sodium salts covered by a straw-colored alcoholic liquid.

The alcohol was distilled off in a vacuum at 27° and 35 mm.

pressure. This distillate contains a small amount of a bromine body, and gives, when boiled with aniline and caustic potash, a strong odor of phenyl isocyanide, indicating the presence of bromated methane derivatives (Bromoform?). The presence of some one of these derivatives is very noticeable when sodium methylate is used in place of sodium ethylate, when there is a very strong and unmistakable smell like bromoform in the flask during the reaction. Boiled down with ammoniacal silver nitrate solution, the distillate gives a silver mirror (aldehyde?), and smells of ethyl carbonate.

After distilling off the main part of the alcohol, the residual red oil, filtered from 54 grams of sodium salts (A) and diluted with 6–8 volumes of ether, gave 14.7 grams more salt (B). An additional 3 grams of salt (C) were obtained by washing the ethereal filtrate from B with a few cc. of water, making a total yield of 71.7 grams (21.7 grams in excess of the theoretical amount of sodium bromide). As this salt contains much carbonate, and the latter fractions (B and C) a considerable amount of a sodium salt of an oily organic acid, the reaction is evidently a very complex one.

The ether solution, thus freed of all inorganic bodies, dried with potassium carbonate, and evaporated in a vacuum, leaves 24 grams of a fragrant red oil.. Distilled in a vacuum it gives:

Fraction I.—4 grams of a fragrant, colorless, refractive oil boiling at 46°–48° under 18 mm. pressure. (An analysis is given below).

Fraction II.—0.5 gram, boiling-point 90°–127°, under 18 mm. pressure.

Fraction III.—2 grams, boiling-point 127°–138°, under 18–16 mm. pressure.

Fraction IV.—13 grams of a thick, colorless oil, distilling at 143°-146° under 16 mm. pressure. In the flask 2.8 grams of a red oil remained.

From Fractions III. and IV. 11 grams of colorless crystals were obtained, which proved to be ethyl diethoxymalonate. These recrystallized from absolute alcohol melt at 43°–44°. (Bischoff 43°–44°). Dried in a vacuum over sulphuric acid and analyzed, they gave the following results:

0.2488 gram of the substance gave 0.4829 gram CO_2, and 0.1811 gram H_2O.

	Theory for $\begin{smallmatrix} C_2H_5O \\ C_2H_5O \end{smallmatrix} > C < \begin{smallmatrix} CO_2C_2H_5 \\ CO_2C_2H_5 \end{smallmatrix}$.	Found.
C	53.23	52.94
H	8.07	8.08

Ethyl diethoxymalonate is a thick, colorless oil, crystallizing on cooling in prisms of the orthorhombic system. The crystals melt at 43°–44°, and distil with little decomposition above 225°. From a saturated alcoholic solution beautiful, transparent plates 3–4 cm. square may be obtained. It is very soluble in alcohol, benzene, chloroform, carbon tetrachloride, acetone and aniline, and difficultly so in ligroïn. The body reduces ammoniacal silver nitrate on long boiling in alcoholic solution, while cold alcoholic sodium ethylate precipitates a white sodium salt. Heated with aniline in sealed tubes at various temperatures up to 270°, it gave no satisfactory results, while some unchanged ester was recovered. It is, therefore, under these conditions, much more stable than the keto ortho esters studied by Claissen.

Fraction I. was redistilled for the third time between 127°–129° at ordinary pressure, and on analysis :

0.1896 gram of the substance gave 0.3428 gram CO_2, and 0.1477 gram H_2O.

	Theory for ethyl carbonate. $(C_2H_5O)_2>CO$.	Found.
C	50.84	49.9
H	8.47	8.6

The low value obtained for carbon is due to the presence of a trace of bromine product, which cannot be removed by repeated distillations. The characteristic odor, boiling-point, analysis, and general properties, leave no doubt, however, that the product is ethyl carbonate (boiling-point, 126°).

36 grams of sodium salt from the above experiment (including all the fractions B and C), shaken with dilute sulphuric acid and ether, gave 8 grams of an oil having a strong smell like acetaldehyde, and reducing ammoniacal silver solution even in the cold. Heated it loses much carbon dioxide at 180°–190°.

A second experiment with ethyl dibrommalonate and sodium ethylate, carried out like the first, except that the reaction-temperature was 10°–15°, gave 65 grams of sodium salts. The amount of carbonate in this salt was apparently much less, and no evolution of free carbon dioxide gas occurred. The ethereal solution gave 16.2 grams of oil, 2.4 grams of which distilled off between 120°–130° at ordinary pressure, and was chiefly ethyl carbonate. The residual oil in the flask gave 4.5 grams of ethyl diethoxymalonate on standing.

A third experiment was made, the conditions of the reaction being the same as in the first, except that 4 atoms of sodium (27.68 grams) were used instead of two, and the temperature was kept at 70°–75°, with a final heating of the flask for ten minutes at 100°. 73 grams of sodium salts containing much carbonate were then separated, and the rest (quantity not determined) finally removed by washing with dilute sulphuric acid and water. The ethereal solution then evaporated on the water-bath gave 19.2 grams of a thin red oil. On distillation 5–6 grams of a low-boiling oil (35°–38° under 47–18 mm.), mostly ethyl carbonate, were obtained. It had, however, a strong aldehyde odor, and reduced ammoniacal silver nitrate solution on warming.

9.6 grams of thick red oil remained in the distilling flask. This gave, on standing for a week at 0°, no sign of ethyl diethoxymalonate crystals.

The effect of reversing the mixing process and dropping the sodium ethylate into the ethyl dibrommalonate, is shown in the following experiment: The temperature of the reaction was 30°–40°, the other conditions being the same as the first experiment. As the addition of sodium ethylate took place bubbles of carbon dioxide gas arose. 57.6 grams of sodium salt were obtained. The ether filtrate evaporated on the water-bath left a fragrant oil, from which, on standing, 5 grams of colorless prismatic crystals of the monoclinic system were obtained. Recrystallized from 70°–80° ligroïn and dried in a vacuum over sulphuric acid, it melted at 56°–57°. The analyses, together with its general properties, prove that it is acetylenetetracarboxylic ethyl ester.

0.1908 gram of the substance gave 0.3728 gram CO_2, and 0.1085 gram H_2O.

	Theory for $(C_2H_5O_2C)_2>C=C<(CO_2C_2H_5)_2$.	Found.
C	53.16	53.29
H	6.33	6.31

The mother-liquor from these crystals distilled at ordinary pressure gave 2 cc. of an oil (boiling-point, 122°–127°), which was chiefly ethyl carbonate. When the temperature of the distilling bath was raised to 280°, no trace of ethyl diethoxymalonate passed over, neither could any crystals of the same be found in the residual brown oil, on standing.

The following table gives a brief summary of the above four experiments:

Experiment.	1.	2.	3.	4.
Temperature	48°–50°	10°–15°	70°–75°	32°–40°
Atoms of sodium used	2	2	4	2
Sodium salts	71.7 gr.	65	73+	57.6
Carbonate present	much	much less than Exp. 1.	large amount	much
Free CO_2 gas	little	none.	large amount	little
Ethyl carbonate	4 gr.	2.4	5–6	2
Crude oil	24	16.2	19.2	not weighed
Ethyl diethoxymalonate	11	4.5	none	none
Acetylenetetracarboxylic ethyl ester	none	none	none	5 grams

Since the appearance of Bischoff's paper on the action of sodium ethylate on ethyl dibrommalonate, I have discontinued the studies along this line. I have shown, however, that operating under more favorable conditions, the yield of ethyl diethoxymalonate is much larger than he obtained. From 95.8 grams ethyl dibrommalonate he obtained 5.9 grams of oil boiling within 20°, *i. e.*, from 240°–260°, but gives no yield of pure crystals, while my yield from the same amount of substance is 15 grams of oil boiling between 127°–146° under 16 mm., yielding 11 grams of pure crystals. I mention this as he explains his low yield on the ground of "unfavorable dynamical conditions." Bischoff makes no statement concerning the formation of ethyl carbonate, free carbon dioxide gas, acetylenetetracarboxylic ethyl ester, or bromated methane derivatives in the reaction.

The fact that acetylenetetracarboxylic ethyl ester is formed by the addition of alcoholic sodium ethylate to ethyl dibrommalonate (Experiment 4) is of interest: it shows that sodium ethylate is capable of removing the bromine from this compound just as Conrad and Brückner[1] have shown is the case on using metallic sodium in benzene solution.

The formation of considerable amounts of free carbon dioxide gas, sodium carbonate and ethyl carbonate (to the largest extent in Experiment 3, temperature 75°, and least in Experiment 2, temperature 10°–15°), shows the easy splitting off of the carboxyl groups. The undoubted presence of bromated methane derivatives would indicate that the loss of carboxyl takes place, at least in part, before the withdrawal of bromine occurs. This peculiar behavior seems analogous to the formation of bromoform by the action of calcium hydroxide or caustic potash solution on dibrommalonamide, as noted by Freund,[2] and the formation of the same body when dibrombarbituric acid is treated with a warm solution of barium hydroxide.[3] The formation of acid oils indicates a saponification of the esters by sodium ethylate, producing sodium salts.

I shall continue experiments, already under way, upon the action of aniline on dibrommalonic acid, mesoxalic ester and acid, and also study further the properties of ethyl dianilidomalonate.

CHICAGO, MAY, 1897.

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[1] Ber. d. chem. Ges., **24**, 3004.

[2] *Ibid.*, **17**, 783.

[3] Baeyer: Ann. Chem. (Liebig), **130**, 134.

THE ACTION OF NITRIC ACID ON TRIPHENYLMETHANE.

BY E. S. SMITH.

The method of preparing trinitrotriphenylmethane by the action of fuming nitric acid on triphenylmethane, is described by Fischer.[1] In an attempt to make this preparation I departed from the exact directions of Fischer and obtained a substance shown by analysis to be triphenylcarbinol, $C.OH.(C_6H_5)_3$. Following are the details of the work: I placed in a flask an unweighed quantity of triphenylmethane recently crystallized from benzene, and probably still retaining a little benzene; poured in an unmeasured quantity of nitric acid (sp. gr. 1.34), and then some fuming nitric acid; allowed the mixture to stand a short time, then heated on the sand-bath for a few minutes. After the reaction was ended a large amount of water was poured in. The reddish-yellow precipitate formed was filtered off on a platinum cone. By pressing down the precipitate a small amount of a red oil, having the smell of nitrobenzene, was forced out. The solid substance was purified by treating it with hot glacial acetic acid, crystallizing it from a mixture of benzene and glacial acetic acid, recrystallizing from benzene, and finally from alcohol. The purified substance is white, resembles triphenylcarbinol, and melts sharply at 161° (uncorr.). A test for nitrogen by the Prussian-blue method, showed absence of nitrogen.

0.138 gram gave 0.0773 gram water, and 0.4458 gram carbon dioxide, indicating the following composition:

	Calculated for triphenylcarbinol.	Found.
C_{19}	87.80	88.10
H_{16}	6.15	6.22
O	6.15	....
	100.00	

Several attempts to confirm this work by repeating it were, on the whole, unsuccessful, though various modifications in the strength of acid, manner of heating, etc., were tried. In one case a very small quantity of a white crystalline substance was obtained which, after recrystallizing from benzene, melted at 161°.

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[1] Ann. Chem. (Liebig), **194**, 254.

Nitric acid of sp. gr. 1.42 does not act upon triphenylmethane until the temperature is raised to about 100°; but the product obtained in this case, as in most of the other experiments, was a waxy substance of salmon color, from which I was not able to get a crystalline compound.

I could find no record of triphenylcarbinol having been made in this manner; the usual method of preparation is to oxidize the triphenylmethane with chromic acid.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY,
BALTIMORE, JUNE, 1897.

REVIEWS.

DAS STUDIUM DER TECHNISCHEN CHEMIE AN DEN UNIVERSITÄTEN UND TECHNISCHEN HOCHSCHULEN DEUTSCHLANDS UND DAS CHEMIKER-EXAMEN. VON PROF. DR. FERD. FISCHER. Braunschweig: Friedrich Vieweg und Sohn. 1897.

In the preface to this short but interesting book, attention is drawn to the fact that there are in Germany but about 200 professional chemists who pursue their studies with a purely scientific aim, while there are about 4000 who devote themselves technically to the various forms of chemical industry. It is to the training of the latter class, 95 per cent. of the whole, —and in Germany only (the Austrian Empire and Switzerland not being included)—that consideration is given by the author.

The marked prominence of the position which Germany has taken in chemical manufactures during the latter half of this century, has attracted great attention in Europe, and is widely recognized on this side of the Atlantic, so that a discussion by so well informed an authority as Prof. Ferd. Fischer of the education of German technical chemists, is well worth reading.

He treats historically of the teaching of chemistry at the German universities, assigning the position of the earliest teacher of chemistry to J. Hartmann, at Marburg, in the early part of the 17th Century, and claiming for Göttingen in the middle and latter part of the 18th Century the first public recognition of chemical technology among university studies. Then is presented a list of the courses now (1895–6) given in chemical technology in the various German universities. Then follows an extended account of the courses of this kind offered at the special polytechnic schools of Germany, and the tests of progress demanded of their students. Next comes a long list of the firms and individuals engaged in the various branches of chemical industry throughout the country, with the dates at which they began work, presenting a striking picture of the development attained within a comparatively short period of the recent past. Such a statement as this—that the *Farbenfabriken*, *vorm. Fr. Bayer & Co.*, in Elberfeld, which, in 1881, employed fifteen chemists and 500 workmen, and in 1896 had 104 chemists and 2644 workmen—justifies the author's exclamation, "*Wahrlich, ein glänzender Aufschwung!*" There is then a lengthy discussion of the desirability of a public, governmental examination for technical chemists, by which their fitness for employment may be tested. This involves consideration of the nature of the preparation which should be aimed at.

The main ideas suggested throughout are, 1st, that the only solid foundation for successful industrial chemistry is a thorough study of chemistry as a science. The author says emphatically: "Die hohe Entwickelung der chemischen Industrie Deutschlands *lediglich dem umfassenden Wissen und Können der deutschen Chemiker zu danken ist*. . . . Nicht *Handarbeit*, sondern *angestrengteste Geistesarbeit* ist hier entscheidend." 2d, that on this must be based, and to this must be added, an extended study of the special conditions involved in profitable work upon the large scale, of the practically available sources of raw materials, of the construction and use of specially devised machinery, of possible channels for the utilization of by-products, of questions of transportation and of markets, of the indirect consequences of changes taking place in any one line of industry, and many other matters which need to be kept in view and seen in their mutual relations, by the man whose education has been that of the true chemist, but is not that of the chemist only. J. W. M.

WATER AND PUBLIC HEALTH: the Relative Purity of Waters from Different Sources. By JAMES H. FUERTES, Member of the American Society of Civil Engineers. New York: John Wiley & Sons. London: Chapman & Hall, limited. 1897.

This little book, of seventy-five pages, aims at a discussion of the character of the water supply, the death-rate from typhoid fever, and the relation of cause and effect between these two, for a number of the larger cities of the world, chiefly in Europe and the United States. Statistics are quoted which have undoubted interest, but the work hardly deserves much praise for the use made of these. There is a lack of clearness. This is partly due to defects in the English employed, as, for example, in the sentence on p. 28, "usually the effect of sedimentation and oxidation have been largely overestimated.'' But the logic, as well as the grammar, may without unfairness be unfavorably criticised: thus, on pp. 22 and 23, the opening sentence of a chapter reads: '' If the drinking water supplied to cities is an index of their healthfulness, as measured by the typhoid fever death-rates, we should expect to find some sort of relation existing between the quality of the water and the typhoid death-rates.'' Exceptions might well be taken to some of the statements as to the sources of water supply of certain cities named, as, for instance, Paris, France, and New Orleans, La. There is no doubt whatever as to the soundness of the general conclusion, that the use of drinking water polluted by decaying organic matter, is habitually accompanied or followed by a high death-rate from typhoid fever. But the author's classification, under eight heads, of special sources of water supply, and the different rates of mortality from typhoid disease which he tries to connect with these, seems much less well established, in view partly of the great complexity of the conditions involved, and partly of the range of variation in each of the classes discussed. A point worth noticing is the apparent greater or less extent of mortality from typhoid fever in certain of the years for which tables are given, irrespective of the localities, and applying alike to widely separated European and American cities. J. W. M.

FRÜHLING UND SCHULZ' Anleitung zur Untersuchung der für die Zucker-Industrie in Betracht kommenden Rohmaterialien, Producte, Nebenproducte und Hülfs-substanzen. 5te, umgearbeitete und vermehrte Auflage, herausgegeben von DR. R. FRÜHLING. Braunschweig: Friedrich Vieweg und Sohn. 1897.

A good example of the full, well arranged, and clearly written manual of the pains-taking German expert in a special field of industrial chemistry. Appearing first some twenty years ago, this work has been carefully worked over in each succeeding edition, until now the fifth is published with judicious omission of matter that has become obsolete, more complete development of what has been retained, and introduction of no small amount of that which is entirely new and valuable.

The chief divisions of the book are the following: The sugars and materials containing sugars, which are of manufacturing interest, including the chemical and physical methods for their examination and quantitative determination; animal charcoal; water; limestone and lime as used in the sugar industry; strontianite and other compounds of strontium; gas (carbon dioxide) used for precipitation; soda and hydrochloric acid used in the treatment of animal charcoal; fuel and fuel gases; *vinasse* from the distillation of molasses spirit; cattle food involving the use of molasses in its preparation; fertilizers and the materials for their manufacture, etc.

As respects intermediate and secondary products, it is the beet sugar industry which has been chiefly kept in view.

There are clear and good engravings in illustration of apparatus and its application, a detailed chapter on reagents and reagent solutions, and a series of twenty-seven useful tables, several of them specially relating to matters connected with the sugar industry. To any one interested in this branch of manufacturing chemistry, the book will be welcome and valuable. J. W. M.

TABELLARISCHE UEBERSICHT DER PYRAZOLDERIVATE. VON DR. GEORG COHN. Braunschweig: Viewig. 1897. pp. 443.

The pyrazol derivatives, of which antipyrine is the best known, have been the subject of a very large number of investigations, and the material accumulated is embarrassingly abundant. The author of this book has brought together all of this material in tabular form, and his work will undoubtedly be of value to those who may have to deal with the compounds of this group. The author says that foreign publications have been treated indirectly through the abstracts found in German journals. That is not a scholarly way of treating them, to say the least.

THE CHLORINATION PROCESS. BY E, B. WILSON, E.M. New York: John Wiley & Sons. London: Chapman & Hall, Limited. 1897. pp. 125. Price, $1.50.

This is a brief, clear account of the chlorination process for treating gold ores. The author claims for the method that "while old, yet it is new;" and that "it has assumed a place in metallurgy from which it cannot be dislodged." Chemists who have not been specially occupied in the field of metallurgy, will find this book interesting and instructive.

TABELLEN FÜR GASANALYSEN, GASVOLUMETRISCHE ANALYSEN, STICKSTOFFBESTIMMUNGEN, etc. VON PROF. DR. G. LUNGE. Braunschweig: Vieweg. 1897.

The well-known tables of Lunge have been prepared in a form adapted to use as charts, the type being large and clear. In this form they will no doubt prove of value to every laboratory.

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CHEMICAL JOURNAL.

THE ACTION OF CARBON DIOXIDE UPON SODIUM ALUMINATE AND THE FORMATION OF BASIC ALUMINIUM CARBONATE.

BY WILLIAM C. DAY.

The literature of aluminium carbonate is intimately associated with that of ferric and chromic carbonates. The existence of carbonate of aluminium and of the corresponding ferric and chromic compounds is referred to as doubtful by high authorities at the present time. The writer cannot help feeling, however, that this doubt is carried further in the minds of many chemists of to-day than a careful study of the literature will justify, and certainly further than the results of experience in connection with the present investigation would warrant. Patents have been issued upon processes for obtaining alumina from sodium aluminate based upon the assumption that carbon dioxide acts at once upon sodium aluminate in the sense of the following equation :

$$Al_2O_2(ONa)_2 + CO_2 + 3H_2O = Al_2(OH)_6 + Na_2CO_3.$$

Thus in a process originally patented by Le Chatelier this reaction is assumed, but in connection with a description of it is the statement that alumina thus precipitated always contains a certain quantity of alkaline carbonate which cannot be removed by washing with water. It may, however, be separated by digestion with the aid of heat in a small quantity of dilute hydrochloric or nitric acid, or by digestion with chloride of aluminium in excess. That the reaction written above does not take place is, I believe, thoroughly proved by the results of the present investigation.

Investigators having for their object the preparation of aluminium carbonate have generally followed the plan of adding alkaline carbonates in solution to solutions of alum or other aluminium salt, and then studying the resulting precipitate. No one, so far as I know, has investigated the product formed by passing carbon dioxide into a cold solution of an alkaline aluminate.

Berzelius[1] says, "if alumina is precipitated by an excess of alkaline carbonates, the precipitate is an insoluble double salt of alkaline carbonate and alumina, which dissolves in acids with effervescence." He, as well as Bucholz before him, doubted the existence of aluminium carbonate.

H. Bley[2] studied the action of alkaline carbonates in excess upon solutions of alum and sulphate of aluminium. According to this writer, either a basic carbonate of aluminium or a double salt of basic aluminium carbonate and the alkaline carbonate employed is obtained. Referring to the assertion that such precipitates continually contain alkaline carbonate mechanically held, he says, "I have convinced myself by the most careful investigation that they are in many cases quite free from alkaline carbonate."

The precipitates studied by Bley were prepared by the use of both ammonium and potassium carbonates. His method of analysis was not clearly shown, but in stating the results he gives the weights of carbon dioxide and alumina only, thus indicating that water was determined by difference.

One preparation gave the following figures:

I. Al_2O_3, 46.70; CO_2, 6.77; $_2O$, 46.53.
II. " 47.80; " 5.50; ' 46.70.

Another preparation (using potassium carbonate) showed the following percentage composition:

I. Al_2O_3, 49.50; CO_2, 6.37; H_2O, 44.12.
II. " 46.00; " 5.27; " 48.73.

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[1] Lehrbuch der Chemie, 5te Aufl. Bd. **3**, 479.

[2] J. prakt. Chem., 1846, **39**, 1.

A third precipitate contained :

I. Al_2O_3, 45.43 ; CO_2, 6.54 ; H_2O, 48.02.
II. " 48.20 ; " 11.39 ; " 40.41.

Inspection of these figures reveals a lack of agreement between two analyses of the same preparation, which is hardly calculated to inspire confidence in either the method of analysis employed or the manipulation.

Bley regards all such precipitates as "mere mixtures."

In 1854 Heinrich Rose published a paper "on the influence of water in chemical decompositions." In this paper reference is made to the work of Muspratt who, without referring to the work of Bley, prepared and analyzed a compound with the following results : Al_2O_3, 44.86 per cent. ; CO_2, 12.91 per cent. ; H_2O, 42.23 per cent.

In the course of his paper, Rose[1] says "it is difficult to see how an alkaline carbonate in solution added to a solution of another salt can be contained mixed in the washed precipitate obtained." Rose obtained the precipitate analyzed by him by treating potassium and ammonium alums mixed in solution with ammonium carbonate in excess. The precipitate was washed with water until the wash-water showed no trace of sulphuric acid. In spite of this, however, on dissolving a sample in dilute hydrochloric acid, a heavy precipitate was obtained with barium chloride. The precipitate was all dissolved in hydrochloric acid, and obtained again by means of ammonium carbonate from this solution. Washing was continued until all traces of sulphuric and hydrochloric acids were removed. Treated with hydrochloric acid, carbon dioxide was freely evolved. On heating, a strong odor of ammonia was produced. Analysis gave the following result from which a formula was deduced :

Al_2O_3, 34.48 ; ammonium oxide, 15.33 ; CO_2, 26.77 ; H_2O, 23.42.

This compound appears then to have been a double carbonate of aluminium and ammonium.

In 1856 M. Langlois[2] published the results of a study of carbonates of aluminium, iron, and chromium. The following quotation from this paper is of much interest: "When we add an alkaline carbonate to a solution of an aluminium salt, a precipitate is obtained and, at the same time, the disengagement of carbon dioxide is observed. It is generally believed that this precipitate is nothing but alumina, still retaining a little alkaline carbonate to which is due the effervesence with acids. I have repeated this experiment, and am assured that by washing with a sufficient quantity of water the precipitate can be entirely freed from alkaline salt. It continues nevertheless to effervesce, which proves that a part of the alumina remains combined with the carbonic acid. The same has been remarked by M. Bley:[1] "There is unquestionably produced a very basic compound of carbonic acid and aluminium hydroxide. This compound is destroyed at a temperature which does not exceed 100°."

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[1] Poggendorf's Annalen, **91**, 452.

[2] Annales d. ch. et d. phys. [3], **48**, 502.

This precipitate, upon analysis, gave the following result:

Al_2O_3, 48.80 per cent.; CO_2, 7.72 per cent.; H_2O, 43.48 per cent.

On the basis of this analysis the following formula was proposed:

$$3(Al_2O_3.CO_2) + 5(Al_2O_3.8HO).$$

Langlois does not appear to have determined each of the three constituents directly; the water seems to have been determined by difference. The operations described seem to have been carried out with great care and thoroughness and the whole investigation seems highly trustworthy.

In 1858 Wallace[2] published the results of an investigation of aluminium, iron, and chromium carbonates. In this he refers to the fact that the existence of such carbonates has been denied by several authorities. The precipitates investigated were prepared by adding sodium carbonate to a dilute solution of aluminium chloride. He emphasizes the tedious character of the work and refers to the time required for washing and drying in terms of weeks. Notwithstanding this protracted washing he was unable to remove all alkali which he assumed to be present in the form of sodium bicarbonate, and calculated his analytical results upon the weight of material taken minus the calculated weight of sodium bicarbonate. Inasmuch as the amount of sodium oxide found is not stated, the reader is left unable to draw any conclusions for himself and the results necessarily lose interest to some extent.

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[1] *Loc. cit.*

[2] Chem. Gazette, **16**, 410.

He concludes from the analysis of several preparations that protracted washing decomposes the aluminium carbonate in some degree.

His analytical results, calculated as explained above, are the following:

Al_2O_3, 56.19; CO_2, 14.26; H_2O, 29.55.

From these figures he calculated the formula,

$$3Al_2O_2.2CO_2 + 9HO = 2(Al_2O_3CO_2 + 3HO) + Al_2O_3.3HO.$$

This formula would require Al_2O_3, 55.04; CO_2, 15.83; H_2O, 29.13 per cent. He explains the deficiency of carbon dioxide in the substance analyzed as due to decomposition from protracted washing.

In 1860 James Barratt[1] investigated the carbonates of aluminium, iron, and chromium.

He refers to the work of Wallace, just considered, also cites Saussure as authority for the belief that the reputed carbonate of aluminium contains no carbon dioxide at all. He claims to have prepared the compound precisely in the same manner as prescribed by Dr. Wallace. After washing it for two days it was dried and analyzed. Three per cent. of carbon dioxide was found. He then triturated it in a mortar with water, placed it upon a filter, and washed further and dried as before over sulphuric acid. Analysis gave these results:

	Calculated for $Al_2(OH)_6$.	Found.
Al_2O_3	65.384	65.03
H_2O	34.616	34.97
CO_2	....	none
	100.000	100.00

Commenting upon these results, he says: "From the above it is evident that when an aluminium salt is precipitated by an alkaline carbonate there is no carbonate of aluminium formed. The three per cent. of carbonic acid found in the first instance was in all probability due to the retention of some of the precipitant (carbonate of soda) by the hydrated alumina."

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[1] Chem. News, 1860, **1**, 110.

His study of the carbonates of iron and chromium showed the presence of carbon dioxide in both, and formulæ including carbon dioxide were calculated for these. The paper concludes as follows :

" The preceding examinations were all most carefully performed under the direction of Dr. Muspratt who, with myself, cannot account for the whole of the carbonic acid being removed from the alumina and not from the other two oxides ; such, however, is the fact as proved by the foregoing experiments, all of which were conducted on the same plan, and each precipitate was apparently submitted to the same conditions and treatment."

In 1862 appeared a publication " On the carbonates of alumina, glucina, and the sesquioxides of iron, chromium, and uranium," by Theodore Parkman.[1] After some difficulty in preparing and washing the precipitates obtained by the action of sodium carbonate upon potassium alum, the author finally adopted the plan of washing with water, saturated with carbonic acid, until a portion of the filtrate, after being boiled to expel carbonic acid, gave no alkaline reaction. This, he says, would probably give correct results since the water being already saturated with carbon dioxide would hardly wash out any from the substance. None of the precipitates were dried before analyzing so that only the percentages of alumina and carbon dioxide were obtainable. The method of analysis was to introduce the substance (which had been previously under pressure between folds of paper for about twelve hours) into a bulb-tube of hard glass. The whole was weighed, connected with a weighed calcium-chloride tube, and ignited in a slow stream of dry air. The loss of weight of the bulb-tube and contents minus the increase of weight of the calcium-chloride tube would give the weight of the carbon dioxide.

The following analyses express merely the ratios of alumina and carbon dioxide, and were obtained simply by adding together the weights of carbon dioxide and alumina and dividing the weight of each constituent by the sum :

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[1] Silliman's Journal, [3], **34**, 321.

	Prep. I.		Prep. II.	Prep. III.		Prep. IV.	
	I.	II.		I.	II.	I.	II.
Al_2O_3	79.13	79.32	79.95	81.37	81.91	77.51	76.72
CO_2	20.87	20.68	24.05	18.63	18.09	22.49	23.28

Commenting upon these figures the author says, "the precipitate by the fixed alkaline carbonates in salts of alumina varies in composition, but approaches the formula $Al_2O_3.CO_2$, and is probably a mixture of this with a more basic salt." While the above figures are interesting, it must be remembered that they represent the partial composition of a wet material, and are therefore scarcely comparable with results obtained from the complete analysis of air-dried substances, such as are treated of in other investigations.

In 1879, Urbain and Renoul[1] published the results of a research "on a compound of alumina with carbonic acid." In the course of the paper appear the following statements: "In the preparation of alumina by means of sodium carbonate and alum, two bodies, very different in appearance, can be obtained according as the precipitation is effected at the boiling-point or at the surrounding temperature. In the first case the precipitate is gelatinous and transparent, and filters with difficulty ; in the second case, on the contrary, it is opaque, and separates from the liquid with the greatest ease. In the dry state the same difference exists. Alumina prepared hot is hard and like horn in appearance ; the alumina obtained cold is pulverulent and perfectly white. Brought in contact with a solution of coloring matter, for example an infusion of campeche wood, the opaque alumina absorbs twice as much coloring matter as the gelatinous.

"When alumina prepared in the cold is treated with an acid it dissolves immediately, giving rise to an abundant liberation of carbonic acid, while alumina precipitated at 100° dissolves only slowly and with no production of gas."

This precipitate was obtained from aluminium sulphate as well as from alum, and by the use of ammonium carbonate instead of sodium carbonate ; the precipitate had the same properties and nearly the same composition, regardless of the method of obtaining it. Dried over sulphuric acid until the weight no longer changed, the substance showed the following composition:

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[1] Comptes rendus, **88**, 1133.

Al_2O_3, 52; CO_2, 11; H_2O, 37, corresponding to the following formula, $CO_2.2Al_2O_3$, 8HO.

"The substance is destroyed by heat; even at 30° it commences to lose its carbonic acid. When it is placed in water and this is warmed, a disengagement of acid is observed, which increases with the temperature, and is complete after boiling some time. Thus, contrary to what has heretofore been supposed, alumina is capable of combining with carbonic acid and forming, it is true, a compound of marked instability."

The observations made in the paper just considered more nearly agree with those made by the writer than the descriptions contained in any other of the publications on the subject.

In 1893 A. Ditte[1] published the results of a study of the action of carbon dioxide upon aluminates of the alkalies in which he obtains crystallized alumina (Gibbsite). He says "when potassium carbonate is added, drop by drop, to a solution of potassium aluminate, a precipitate forms which at first redissolves, but afterwards becomes permanent; it has perhaps the composition $3K_2O.Al_2O_3.5CO_2$." No analyses of the compounds are given and the reasons for ascribing this formula to the precipitate do not appear in the paper. The following explanation of the action of carbon dioxide upon alkaline aluminate is of interest. "If carbonic anhydride is passed into a solution of potassium aluminate containing a small excess of alkali until a permanent precipitate of the double carbonate and the crystallized hydroxide begins to form, and the flask is then closed, a heavy precipitate of the double carbonate at first settles out, but this is gradually decomposed by the potassium hydroxide liberated by the decomposition of the aluminate by water, and crystallized aluminium hydroxide separates. If the solution contains a considerable excess of alkali, and carbonic anhydride is passed into it until a permanent precipitate begins to form, and the flask is then closed, a precipitate of the double carbonate separates, but, as there is still sufficient potassium hydroxide in the liquid to prevent decomposition of the aluminate, crystallized aluminium hydroxide is not formed.'' This paper is interesting and suggestive, but it does not deal directly with the issues of the present investigation, inasmuch as no analyses of precipitates obtained are given, and the question of the existence of carbonate of aluminium is not considered as a distinct issue.

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[1] Comptes rendus, **116**, 183–185 and 386–388.

Some time ago, being desirous of obtaining pure alumina by the action of carbon dioxide upon sodium aluminate, the writer carried out some experiments with this end in view and, in the course of the work, became thoroughly impressed with a sense of the difficulty of washing the precipitated alumina free from alkaline carbonate, and also by the observation that the precipitate did not look like ordinary alumina in that it appeared somewhat less gelatinous or rather more granular, and that its color was a more opaque white than that of alumina as obtained by precipitation by ammonia from alum or other aluminium salt. It seemed, therefore, advisable to carry out a series of experiments with the object of determining by quantitative analysis the exact nature of the carbon dioxide precipitate after it had been washed until water would remove nothing more. Consultation of a number of reference works, including Watts' Dictionary, showed that the existence of carbonate of aluminium was a matter of doubt. No further study of the literature was undertaken until the investigation was finished.

The sodium aluminate employed was obtained from a natural phosphate of iron and aluminium known by the tradename of ''Connetable'' phosphate rock. This was treated with quicklime and sodium carbonate in the presence of water sufficient to form a thick mud, and the resulting sodium aluminate was afterwards washed out, leaving all iron compounds and phosphate of calcium undissolved, the aluminate containing no trace of phosphoric acid. Carbon dioxide was then freely passed through the solution of aluminate until no more precipitate resulted.

Before taking up these experiments a specimen of alumina, described in the catalogue of a dealer in chemicals as "alumina soluble in acids," was studied. This, on treatment with dilute acids, dissolved promptly but with liberal effervescence. The method of analysis followed in this and all other cases consisted in heating the substance in a combustion tube placed in a combustion furnace. The water and carbon dioxide expelled by heat were absorbed in weighed calcium-chloride tubes and caustic-potash bulbs, respectively, placed just as in the determination of hydrogen and carbon in an organic analysis. Alumina was in all cases determined by dissolving the original substance in acid and precipitating aluminium hydroxide by means of ammonia in the customary manner. Sodium was determined by evaporating the filtrate from the alumina to dryness, and weighing finally as sodium sulphate, or by determining volumetrically the chlorine present in combination with sodium as sodium chloride and calculating the sodium corresponding thereto.

Analysis of Commercial Alumina "Soluble in Acids."

I. 0.5036 gram substance gave 0.1351 gram CO_2, and 0.1029 gram H_2O.

II. 0.2487 gram substance gave 0.0645 gram CO_2, and 0.0498 gram H_2O.

III. 0.2231 gram substance gave 0.07126 gram Al_2O_3, and 0.1097 gram Na_2SO_4.

IV. 0.2180 gram substance gave 0.6826 gram Al_2O_3, and 0.1055 gram Na_2SO_4.

	I.	II.	III.	IV.
CO_2	26.83	25.93	....	....
H_2O	20.43	20.02	....	....
Al_2O_3	....	....	31.94	31.31
Na_2O	....	....	21.47	21.12

Averaging these results we have the following composition for alumina "soluble in acids:"

	Per cent.
CO_2	26.38
H_2O	20.23
Al_2O_3	31.63
Na_2O	21.30
	99.54

Evidently alumina is a misnomer for such a mixture as is indicated by these figures.

Ten grams of this material were then washed with boiling water until the washings gave no alkaline reaction with litmus or phenol phthaleïn. The residue from this washing effervesced upon treatment with dilute hydrochloric acid, but it did not dissolve so completely as before washing, nor could it be entirely dissolved by dilute acid even upon heating.

After drying upon the water-bath it was analyzed:

I. 0.2129 gram substance gave 0.0366 gram CO_2, and 0.0471 gram H_2O.

II. 0.2062 gram substance gave 0.0361 gram CO_2, and 0.0464 gram H_2O.

III. 0.2105 gram substance gave 0.10276 gram Al_2O_3, and 0.0562 gram Na_2SO_4.

IV. 0.2169 gram substance gave 0.10616 gram Al_2O_3, and 0.0635 gram Na_2SO_4.

	I.	II.	III.	IV.
CO_2	17.19	17.51	....	....
H_2O	22.12	22.50	....	....
Al_2O_3	....	....	48.82	48.94
Na_2O	....	....	11.66	12.78

Averaging these we have:

CO_2	17.35
H_2O	22.31
Al_2O_3	48.88
Na_2O	12.22
	100.76

The amount of carbon dioxide required by 12.22 parts by weight of sodium oxide to form sodium bicarbonate is 17.34. The substance having been washed with hot water it seems strange that sodium bicarbonate should have survived such treatment. As is well-known, it is difficult to preserve sodium bicarbonate even at ordinary temperatures, without partial decomposition into the normal carbonate. The question naturally arises, Is the carbon dioxide here present held in combination by the oxide of sodium only, or does the weak base alumina also play a part in this?

Preparation A from Connetable Phosphate Rock.

This was made by heating powdered Connetable rock with quicklime and sodium carbonate in the presence of enough water to form a thick mud, and subsequently washing out the sodium aluminate thus formed with hot water. The solution so obtained contained no trace of phosphoric acid. It was poured into bottles and a rapid current of carbon dioxide was passed through the cold liquid until no alumina could be found in the solution.

After the carbon dioxide had been passing through the solution for some little time a precipitate began to form; this could at first be redissolved by shaking, but later it became permanent. The precipitate settled quite readily, and differed from aluminium hydroxide, precipitated by ammonia from a solution of an aluminium salt, in that it was of an opaque white color and more granular or less gelatinous than the hydroxide as ordinarily obtained. The precipitate was washed with hot water upon the filter, after which it was dried on the water-bath. The dried substance was then washed with hot water by decantation until the washings were no longer alkaline. After drying again on the water-bath, treatment of a portion with hydrochloric acid caused effervescence, and washing with hot water produced an alkaline filtrate. It was evident that drying on the water-bath had had the effect of rendering alkaline matter soluble, since, before this drying, no alkali was detected in the wash-water. Washing was again resorted to; the substance was shaken with hot water, and allowed to settle twenty-four times before a neutral filtrate was obtained. After a final drying on the water-bath, it still effervesced with dilute hydrochloric acid. Subjected to analysis it gave the following results:

I. 0.5026 gram substance gave 0.1231 gram CO_2, and 0.1122 gram H_2O.

II. 0.2396 gram substance gave 0.0598 gram CO_2, and 0.0507 gram H_2O.

III. 0.2012 gram substance gave 0.07636 gram Al_2O_3, and 0.0794 gram Na_2SO_4.

IV. 0.5043 gram substance gave 0.19206 gram Al_2O_3, and 0.2030 gram Na_2SO_4.

	I.	II.	III.	IV.
CO_2	24.49	24.95	....	....
H_2O	22.32	21.16	....	....
Al_2O_3	....	....	37.95	38.08
Na_2O	....	....	17.19	17.57

Averaging the results, we obtain for preparation *A* the following percentage composition :

	Per cent.
CO_2	24.72
H_2O	21.74
Al_2O_3	38.02
Na_2O	17.38
	101.86

The amount of carbon dioxide required by 17.38 parts of sodium oxide is 24.66, if we assume that the carbon dioxide present is combined only with oxide of sodium to form sodium bicarbonate ; this is very nearly the amount of carbon dioxide actually found, but, as in the preceding preparation, it seems strange that sodium bicarbonate should be able to withstand such protracted washing with hot water as well as repeated drying at the temperature of boiling water.

Preparation B from Connetable Rock.

Wishing to avoid any decomposition such as might be caused by heat, it was decided at this point to conduct all washings of the precipitated alumina with cold water, and to allow the completely washed precipitate to dry in the air without any heating whatever. The material was prepared from Connetable rock in the same manner as *A*. After siphoning off the clear liquid from the carbon dioxide precipitate, the latter was washed with cold water by decantation. During the first two washings the precipitate settled rapidly and completely ; at the third addition of water it settled much more slowly and, even after standing over night, it had not settled entirely, but the supernatant liquid was slightly turbid. After three more washings it again settled quickly and perfectly. This stage of slow settling was noticed in all the subsequent preparations, *i. e.*, they settled quickly and perfectly for the first three or four washings, then much more slowly and less perfectly for several washings, after which rapid and complete settling again took place. After seven washings, phenol phthaleïn gave no indication of alkalinity in the wash-water; the precipitate was then drained off, and spread out in the air to dry. When perfectly dry, it was powdered and analyzed with the following results:

I. 0.1485 gram substance gave 0.0130 gram CO_2, and 0.0588 gram H_2O.

II. 0.2090 gram substance gave 0.0195 gram CO_2, and 0.0817 gram H_2O.

III. 0.1088 gram substance gave 0.0099 gram CO_2, and 0.0425 gram H_2O.

IV. 0.1571 gram substance gave 0.0771 gram Al_2O_3, and 0.0107 gram Na_2SO_4.

V. 0.1657 gram substance gave 0.0824 gram Al_2O_3, and 0.0080 gram Na_2SO_4.

VI. 0.1704 gram substance gave 0.0850 gram Al_2O_3, and 0.0091 gram Na_2SO_4.

	I.	II.	III.	IV.	V.	VI.
CO_2	8.75	9.33	9.1	....	....	....
H_2O	39.59	39.09	39.06	....	....	....
Al_2O_3	....	....	....	49.08	49.73	49.88
Na_2O	....	....	....	2.97	2.11	2.33

From an average of these results the following percentage composition is indicated.

CO_2	9.06
H_2O	39.25
Al_2O_3	49.56
Na_2O	2.47
	100.34

This preparation dissolved promptly and completely in dilute acid, and with effervescence.

The 2.47 per cent. of sodium oxide here present require, in order to form sodium bicarbonate, 3.51 per cent. of carbon dioxide, whereas the amount of carbon dioxide actually present is 9.06 per cent., or 5.55 more than the maximum with which the sodium oxide is capable of combining. There seems to be no way of avoiding the conclusion that in this compound

5.55 per cent. of carbon dioxide is held in combination by alumina, and that we have in this material either a basic double carbonate of sodium and aluminium or aluminium carbonate mixed with other compounds.

Preparation C from Connetable Rock.

This was made according to the method adopted for *A* and *B*. As in the case of *B*, washing was done with cold water only, and the material was air-dried. The precipitate settled promptly, leaving the wash-water perfectly clear for the first four washings; then, as in the other cases, it reached the slow-settling stage, when for three washings it settled very slowly, after which it again settled promptly each time. When phenol phthaleïn failed to indicate alkalinity of the wash-water, the material was drained off and dried by standing in the air. Analysis gave the following results:

I. 0.2148 gram substance gave 0.0304 gram CO_2, and 0.0762 gram H_2O.

II. 0.2370 gram substance gave 0.0334 gram CO_2, and 0.0854 gram H_2O.

III. 0.2263 gram substance gave 0.09566 gram Al_2O_3, and 0.0400 gram Na_2SO_4.

IV. 0.2137 gram substance gave 0.09116 gram Al_2O_3, and 0.0375 gram Na_2SO_4.

	I.	II.	III.	IV.
CO_2	14.15	14.09	....	....
H_2O	35.47	36.03	....	....
Al_2O_3	....	....	42.27	42.66
Na_2O	....	....	7.72	7.66

Averaging, the composition appears to be:

CO_2	14.12
H_2O	35.75
Al_2O_3	42.47
Na_2O	7.69
	100.03

The 7.69 per cent. of sodium oxide present require 10.91 per cent. of carbon dioxide to form sodium bicarbonate; evidently there is an excess above this quantity of 3.21 per cent.

Here then, as in the case of preparation *B*, the aluminium must assist in holding the carbon dioxide in combination.

Preparation D from Connetable Rock.

At this stage of the investigation it seemed important to carry the washing of the precipitates to the utmost perfection attainable, in the hope of getting a substance which should contain no sodium whatever. The test of complete washing up to this time had been the absence of any effect upon phenol phthaleïn by the cold wash-water decanted from the precipitate. Frequently also the wash-water was evaporated to dryness on the water-bath and, if any residue at all was left, it amounted to so little toward the end of the washing that the rule of boiling to expel carbon dioxide in the phenolphthaleïn test had not been uniformly observed. From this time on the test consisted in adding a few drops of a solution of phenol phthaleïn, and invariably boiling to expel traces of carbon dioxide; the washing was discontinued only when not the faintest trace of pink color was discernible.

To fulfil this requirement, more washings became necessary but with the result, as will be seen, that the sodium was all but completely removed while the carbon dioxide did not fall below 4 per cent. in any case, and, in three of the four remaining cases, amounted to about 8 per cent.

Preparation *D* was made in the manner already described for *A*, *B*, and *C*. Instead of washing in open cylinders, however, glass-stoppered bottles were used; for some reason the precipitates settled throughout the series of washings more slowly than any of the preceding preparations, passing however, as the others had done, through the specially slow-settling stage. This preparation was washed twenty-four times; many of the settlings required ten hours, and some more than this. After drying in the air, analysis gave the following results:

I. 0.2369 gram substance gave 0.0206 gram CO_2, and 0.1188 gram H_2O.

II. 0.2320 gram substance gave 0.0188 gram CO_2, and 0.1159 gram H_2O.

III. 0.4215 gram substance gave 0.1716 gram Al_2O_3.

IV. 0.2238 gram substance gave 0.0895 gram Al_2O_3.

V. 0.3371 gram substance gave 0.1379 gram Al_2O_3.

VI. 0.2818 gram substance gave 0.0062 gram Na_2SO_4.

VII. 0.2158 gram substance gave 0.0070 gram Na_2SO_4.

	I.	II.	III.	IV.	V.	VI.	VII.
CO_2	8.69	8.10	....	....	....	....	....
H_2O	50.15	49.95	....	....	....	....	....
Al_2O_3	....	....	40.71	40.00	40.91	....	....
Na_2O	....	....	....	....	....	0.96	1.41

Averaging these determinations we have :

CO_2	8.39
H_2O	50.05
Al_2O_3	40.54
Na_2O	1.18
	100.16

The maximum amount of carbon dioxide which the 1.18 per cent. of sodium oxide can combine with is 1.67 per cent ; there is present in the compound 6.72 per cent. of carbon dioxide in excess of this amount. This substance appears to be a highly basic carbonate of aluminium aside from the small percentage of sodium oxide found.

Preparation E from Connetable Rock.

This was made in the usual manner. Until the sixth washing the precipitate settled quickly and perfectly ; after this it settled very slowly, taking ten days to settle between the eighth and ninth washings. After the ninth washing no alkali could be detected in the wash-water. The material was air-dried and analyzed.

I. 0.2197 gram substance gave 0.0192 gram CO_2, and 0.0928 gram H_2O.

II. 0.2149 gram substance gave 0.0202 gram CO_2, and 0.0910 gram H_2O.

III. 0.2053 gram substance gave 0.1017 gram Al_2O_3.

IV. 0.2039 gram substance gave 0.1023 gram Al_2O_3.

V. 0.2053 gram substance gave NaCl corresponding to 0.000403 gram Cl (volumetrically determined). Strength of $AgNO_3$ solution, 1 cc. = 0.000982 gram Cl.

VI. 0.2039 gram substance gave NaCl corresponding to 0.000689 gram Cl.

	I.	II.	III.	IV.	V.	VI.
CO_2	8.74	9.39	....	....	....	....
H_2O	42.24	42.34	....	....	....	....
Al_2O_3	....	....	49.54	50.17	....	....
Na_2O	....	....	....	....	0.17	0.29

Averaging these figures we have :

CO_2	9.06
H_2O	42.29
Al_2O_3	49.85
Na_2O	0.23
	101.43

Neglecting the small amount of sodium oxide present, this preparation, like the preceding, is a highly basic carbonate of aluminium.

Preparation F from Connetable Rock.

This was made in the same way as the preceding. It was washed and allowed to settle 33 times, when the wash-water no longer had an alkaline reaction. After drying in the air it was analyzed.

I. 0.2333 gram substance gave 0.0177 gram CO_2, and 0.0909 gram H_2O.

II. 0.2053 gram substance gave 0.0155 gram CO_2 and 0.0809 gram H_2O.

III. 0.2075 gram substance gave 0.1103 gram Al_2O_3.

IV. 0.1979 gram substance gave 0.1042 gram Al_2O_3.

V. 0.1680 gram substance gave 0.0893 gram Al_2O_3.

VI. 0.1501 gram substance gave 0.0794 gram Al_2O_3, and 0.0040 gram Na_2SO_4.

	I.	II.	III.	IV.	V.	VI.
CO_2	7.59	7.55	....	....	....	....
H_2O	38.96	39.41	....	....	....	....
Al_2O_3	....	....	53.16	52.65	53.15	52.90
Na_2O	....	....	....	....	....	1.16

Averaging these we have :

CO_2	7.57
H_2O	39.18
Al_2O_3	52.96
Na_2O	1.16
	100.87

Again, in this compound we have the conditions required by a highly basic carbonate of aluminium.

Preparation G from Connetable Rock.

This was prepared, washed, and dried in the same manner as the preceding preparations.

Analysis:

I. 0.2280 gram substance gave 0.0097 gram CO_2, and 0.0796 gram H_2O.

II. 0.2353 gram substance gave 0.0088 gram CO_2, and 0.0822 gram H_2O.

III. 0.1636 gram substance gave 0.0998 gram Al_2O_3, and NaCl corresponding to 0.000638 gram Cl (volumetrically determined).

	I.	II.	III.
CO_2	4.25	3.74	....
H_2O	34.91	34.93	....
Al_2O_3	....	....	61.00
Na_2O	....	....	0.34

Averaging these figures we have:

CO_2	3.99
H_2O	34.92
Al_2O_3	61.00
Na_2O	0.34
	100.25

This compound is not far removed in composition from aluminium hydroxide, $Al_2(OH)_6$.

Summary of Analytical Results Obtained in this Investigation.

	Acid-soluble, commercial alumina, after washing.	A.	B.	C.	D.	E.	F.	G.
CO_2	17.35	24.72	9.06	14.12	8.39	9.06	7.57	3.99
H_2O	22.31	21.74	39.25	35.75	50.05	42.29	39.18	34.92
Al_2O_3	48.88	38.02	49.56	42.47	40.54	49.85	52.96	61.00
Na_2O	12.22	17.38	2.47	7.69	1.18	0.23	1.16	0.34
	100.76	101.86	100.34	100.03	100.16	101.43	100.87	100.25

Summary of Results by Previous Investigators.

		Bley.[1]		Muspratt.[2]	Rose.[3]	Langlois.[4]	Wallace.[5]	Barratt.[6]	Urbain and Renoul.[7]
		I.	II.						
CO_2	6.14	5.82	8.97	12.91	26.77	7.72	14.26	none	11
H_2O	40.62	46.43	44.22	42.23	23.42	43.48	29.55	34.97	37
Al_2O_3	47.25	47.75	46.82	44.86	34.48	48.80	56.19	65.03	52
$(NH_4)_2O$	....	....	....	....	15.33	....	....	....	..

In view of the results obtained in this investigation, it hardly seems reasonable to continue a denial of the existence of at least a basic carbonate of aluminium.

Furthermore, there seem to be double carbonates of alumina and the alkalies, as indicated by the conduct and the analyses of "commercial alumina after washing," and preparation *A*, from both of which apparently even hot water would not wash out any more alkaline matter. Preparations *B* to *G*, both inclusive, are substances which contain an excess of carbon dioxide well above the maximum amount with which the sodium oxide present is capable of combining.

In the case of preparations *D* to *G*, both inclusive, the amounts of sodium oxide present are very small, so that it must be concluded that these bodies either are, or at least contain, basic carbonate of aluminium. Preparation *G* is but slightly removed in composition from the hydroxide, $Al_2(OH)_6$, and probably longer continued treatment with water would have converted it entirely into the hydroxide. It will be remembered that Barratt found 3 per cent. of carbon dioxide in the preparation analyzed by him; he ascribed it to alkaline carbonate still to be washed out, but it is not improbable that the substance was similar to preparation *G*; he did not analyze it fully but continued washing, ultimately obtaining the hydroxide.

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[1] Different analyses of the same preparation showed poor agreement. Methods of analysis are not definitely stated.

[2] Method of analysis not stated. Barratt's work was done under Muspratt's direction, and the latter makes no attempt to explain his previous results, but apparently accepts Barratt's conclusions as final.

[3] No one else found ammonia present when the precipitate was formed by ammonium carbonate.

[4] Water apparently determined by difference.

[5] Wallace did not wash entirely free from alkali and calculated results after subtracting calculated weight of sodium bicarbonate assumed to be present.

[6] Barratt at first found 3 per cent. of CO_2 but, after more washing, obtained $Al_2(OH)_6$. He very probably decomposed a carbonate of aluminium by protracted washing.

[7] Figures given only in round numbers.

Of considerable interest in this connection is the mineral hovite discovered and analyzed by J. H. and G. Gladstone[1] and described in Dana's Mineralogy, p. 709.

The following are analyses of the mineral collyrite, associated with which hovite occurs; the samples include hovite:

	SO_2.	CO_2.	Al_2O_3.	CaO.	H_2O.
I.	6.22	10.91	41.04	7.37	33.16 = 98.70
II.	5.87	14.77	39.58	11.22	28.56
III.	5.41	18.15	36.32	11.62	29.16
IV.	5.30	14.14	40.51	9.18	30.87

In I. the 7.37 per cent. calcium oxide present require 11.6 per cent. of carbon dioxide to form calcium bicarbonate; this is only slightly in excess of the amount actually present.

II. requires 17.6 per cent. of carbon dioxide to form bicarbonate of calcium, III. 18.26, and IV. 14.4 per cent.

The following is quoted from Dana's Mineralogy: "J. H. and G. Gladstone state that there is carbonic acid enough in the collyrite to form a bicarbonate with the lime present; but this view of the composition is set aside because of the solubility of the so-called bicarbonate, and its being unknown in the solid state; and hence they suggest that the excess of carbonic acid may be combined in the mineral with alumina, making a hydrous carbonate of alumina and lime, or perhaps replaces part of the silica in the alumina silicate.

"But although the bicarbonate referred to is known only in solution, the most likely condition for finding it in the mineral kingdom is in one of the hydrous silicates of alumina, like collyrite, in which there is present much water, loosely held; the mineral therefore is most probably a carbonate of the formula above given; especially since *a carbonate in which* Al_2O_3 *or* Fe_2O_3 *enters is, as the authors admit, yet unknown to chemistry.*"[2]

In view of the facts developed in the present investigation, it seems highly probable that the mineral, instead of being a bicarbonate, is really a basic double carbonate of aluminium and calcium.

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[1] Phil. Mag., IV., **23**, 462, 1862.

[2] The italics are mine.—W. C. D.

In carrying out this investigation I have had the assistance of three of my pupils, Miss Altha T. Coons, Mr. Clarence B. Hoadley, and Mr. Reuben G. Bennett. The work has presented a number of tedious and trying features, and I feel much indebted to my assistants for the unflagging zeal which they have shown throughout.

SWARTHMORE COLLEGE, PA.,
May 25, 1897.

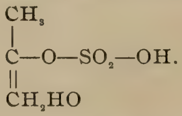
ALIPHATIC SULPHONIC ACIDS.

I.—(1, 2)-ETHANEDISULPHONIC ACID.

BY ELMER. P. KOHLER.

The work described in this paper is the result of an effort to find general methods for the preparation of unsaturated aliphatic sulphonic acids, and particularly of isomeric sulphonic acids analogous to fumaric and maleïc acids.

Only two unsaturated sulphonic acids have hitherto been described. The first was obtained by Schrohe,[1] by passing allylene into sulphuric acid and boiling the product with water. The product was isolated and analyzed in the form of the barium salt, and was not further studied. According to later work by Orndorff and Young[2] the acid is not an unsaturated sulphonic acid but probably isopropenylsulphuric acid,



$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{C—O—SO_2—OH.} \\ \| \\ \mathrm{CH_2HO} \end{array}$$

The second was prepared by Rad[3] by boiling allyl iodide with potassium sulphite. It was isolated, only in the form of complex double salts from which it was impossible to obtain either the free acid or any simple derivatives of it. I have found that unsaturated sulphonic acids can be prepared by a number of the methods available for the preparation of unsaturated compounds. All of these methods, however, meet with the difficulties encountered by Rad; either the unsaturated sulphonic acid is destroyed almost as fast as formed, or it is obtained in the form of double salts from which it is difficult, or impossible, to isolate the free acid. Thus every effort to realize the reaction represented by the equation

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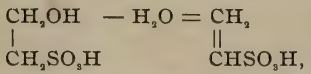
[1] Ber. d. chem. Ges., **18**, 18 and 367.

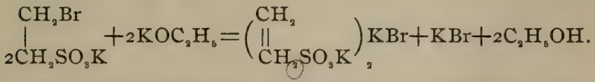
[2] This JOURNAL, **15**, 273.

[3] Ann. Chem. (Liebig), **161**, 218.



$$\begin{array}{l} CH_2OH \\ | \\ CH_2SO_3H \end{array} - H_2O = \begin{array}{l} CH_2 \\ \| \\ CHSO_3H, \end{array}$$

resulted in a complete decomposition of the sulphonic acid. It is comparatively easy, on the other hand, to split off hydrobromic acid from (1, 2)-bromsulphonic acids. The product, however, is always one or more double salts. From (1, 2)-monobromethanesulphonic acid, for example, a double salt of ethylenesulphonic acid is obtained according to the reaction:



$$\begin{array}{l} CH_2Br \\ | \\ 2CH_2SO_3K \end{array} + 2KOC_2H_5 = \left(\begin{array}{l} CH_2 \\ \| \\ CH_2SO_3K \end{array}\right)_2 KBr + KBr + 2C_2H_5OH.$$

The result is the same when Strecker's reaction is applied to the halogen substitution-products of unsaturated hydrocarbons. Thus monobromethylene gives, with potassium sulphite, the same salt that was obtained from (1, 2)-monobromethanesulphonic acid,

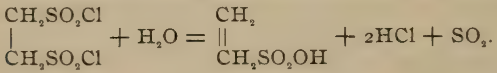
$$2CH_2{=}CHBr + 2K_2SO_3 = (CH_2{=}CHSO_3K)_2KBr + KBr.$$

These double salts are extremely stable; they can be boiled with lead acetate for days without complete precipitation of all the halogen present. They are readily decomposed by warming with concentrated sulphuric acid, but under these conditions they also readily take up water and pass into saturated oxysulphonic acids:

$$2(CH_2{=}CHSO_3K)_2KBr + 4H_2O + 3H_2SO_4 = \\ 4CH_2OHCH_2SO_3H + 3K_2SO_4 + 2HBr.$$

The result, therefore, is a mixture of sulphonic acids, which it is extremely difficult to separate. In the case of unsaturated disulphonic acids, of the fumaric acid type, Strecker's reaction fails altogether, since the dihalogen addition-products of the acetylene hydrocarbons do not react with sulphites.

No better results are obtained by direct reaction between acetylene hydrocarbons and sulphuric acid. Acetylene hydrocarbons are readily absorbed by sulphuric acid and, after warming, the solution always contains some unsaturated sulphonic acid. These unsaturated acids are so easily oxidized, however, that the yield of pure acid ultimately obtained is always small. The unsatisfactory yield obtained by all the methods described above, led to an attempt to prepare unsaturated sulphonic acids by splitting off sulphur dioxide from saturated polysulphonic acids. It has frequently been observed that unsaturated acids and alcohols combine directly with acid sulphites, to form saturated sulphonic acids. Thus, sulphosuccinic acid was obtained by Credner[1] by direct addition of acid sulphites to fumaric acid, and by Messel[2] by the addition of the same substance to maleïc acid. It seemed probable, therefore, that under suitable conditions, sulphurous acid could be split off from sulphonic acids. This, in the case of polysulphonic acids, ought to give unsaturated sulphonic acids. I selected (1, 2)-ethanedisulphonic acid for study, because it is readily obtained in quantity. I found that the diacid chloride of this substance loses sulphur dioxide and hydrochloric acid with the greatest ease, and passes into an unsaturated sulphonic acid. Thus by simply boiling the chloride with water the greater part of it is converted into ethylenesulphonic acid—the lowest member of the unsaturated aliphatic sulphonic acids—according to the equation :



$$\begin{matrix} CH_2SO_2Cl \\ | \\ CH_2SO_2Cl \end{matrix} + H_2O = \begin{matrix} CH_2 \\ \| \\ CH_2SO_2OH \end{matrix} + 2HCl + SO_2.$$

To determine to what extent this reaction can be used for the preparation of unsaturated sulphonic acids, twenty-three sulphonic acids were studied with reference to their behavior towards phosphorus pentachloride, and with reference to the behavior of the resulting chloride towards water. The general results—to which there are no exceptions in the case of the acids studied—were as follows :

1. Monosulphonic acids and (1, 1)-chlor- or brommonosubstitution-products of monosulphonic acids react readily with phosphorus pentachloride in the cold. The product is a nor-

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[1] Ztschr. Chem. [2], **6**, 77.

[2] *Ibid*, [2], **6**, 459; and Ann. Chem. (Liebig), **157**, 15.

mal sulphone chloride, which, when decomposed with water, passes back into the acid :

(1) $C_2H_5SO_3K + PCl_5 = C_2H_5SO_2Cl + POCl_3 + KCl.$
(2) $C_2H_5SO_2Cl + H_2O = C_2H_5SO_2OH + HCl.$
(3) $CH_3.CHBrSO_3K + PCl_5 = CH_3CHBrSO_2Cl +$
$POCl_3 + KCl.$
(4) $CH_3CHBrSO_2Cl + H_2O = CH_3CHBrSO_3H + HCl.$

2. (1, 2)-Chlorsulphonic acids, and (1, 2)-bromsulphonic acids likewise react with phosphorus pentachloride in the cold. When the sulphone chloride thus obtained is boiled with water, two reactions take place. Most of the chloride passes back into the acid. A small quantity of the chloride, however, reacts so as to form an unsaturated sulphonic acid :

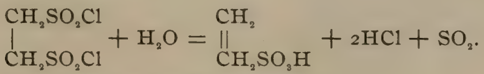
$$CH_2BrCH_2SO_2Cl + H_2O = CH_2{=}CHSO_2H + HCl + HBr.$$

3. (1, 1)-Disulphonic acids do not react with phosphorus pentachloride in the cold. The product, on heating, is mainly a (1, 1)-chlorsulphone chloride,

$$CH_2(SO_3K)_2 + 2PCl_5 = CH_2ClSO_2Cl + 2POCl_3 + 2KCl + SO_2.$$

Other chlorine substitution-products are, however, generally formed at the same time. Thus, (1, 1)-ethanedisulphonic acid gives (1, 1)-chlorethanesulphone chloride, (2)-chlor-(1, 1)-chlorethanesulphone chloride, and (1, 1)-dichlorethane.

4. (1, 2)-Disulphonic acids do not react with phosphorus pentachloride in the cold. On heating, a disulphone chloride is formed which reacts with water in two different ways. The main reaction always results in the formation of an unsaturated sulphonic acid :



$$\begin{array}{l} CH_2SO_2Cl \\ | \\ CH_2SO_2Cl \end{array} + H_2O = \begin{array}{l} CH_2 \\ \| \\ CH_2SO_3H \end{array} + 2HCl + SO_2.$$

A minor reaction regenerates the acid.

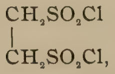
5. (1, 1)-Sulphocarbonic acids and (1, 2)-sulphocarbonic acids slowly react with phosphorus pentachloride in the cold. The product is always a chlorine substitution-product of a diacid chloride. The reaction of this product with water is generally complicated, and appears to be different in different

cases. Among the products there is always an unsaturated sulphonic acid.

These results, which will be treated in detail in subsequent papers, show that whenever an unsaturated acid is formed by the decomposition of a chloride of a saturated acid, with water, two reactions take place side by side; the one resulting in the regeneration of the saturated acid, the other in the formation of an unsaturated acid. To determine what conditions are most favorable to the one or the other of these reactions I studied the behavior of (1, 2)-ethanedisulphone chloride towards a number of different reagents, and under a variety of different conditions. The results obtained form the special subject of this paper.

(1, 2)-ETHANEDISULPHONIC ACID.

(1, 2)-Ethanedisulphonic acid was first obtained by Buckton and Hofmann[1] by the action of fuming sulphuric acid on propionitrile. These investigators studied only the free acid and a few of its salts. Some years later Königs[2] prepared the chloride by treating the sodium salt with phosphorus pentachloride. He assigned to it the symmetrical formula



$$\begin{array}{l} CH_2SO_2Cl \\ | \\ CH_2SO_2Cl, \end{array}$$

and showed that by the action of phosphorus pentachloride the two sulphonic acid residues can be successively replaced by chlorine. Königs also observed that when the alcoholic solution of the chloride is boiled sulphur dioxide is evolved. More recently, Otto[3] and Casanova reduced the chloride with zinc dust and water, and obtained the corresponding sulphinic acid. Beyond this nothing is known either of the acid or of its derivatives.

I. Preparation of Materials.

1. Sodium Ethanedisulphonate.—The sodium salt of (1, 2)-ethanedisulphonic acid is readily prepared by boiling ethylene bromide with sodium sulphite in concentrated aqueous solution and recrystallizing the product from water. It is considerably less soluble than sodium bromide and forms no double salts, hence Beilstein's modification of Strecker's reaction offers no advantages. The yield is almost quantitative if the sulphite is used in sufficient excess and the solution kept concentrated. In more dilute solutions only one of the bromine atoms of ethylene bromide is replaced, and sodium monobromethanesulphonate is obtained. This is slowly decomposed by boiling water with formation of sodium isethionate:

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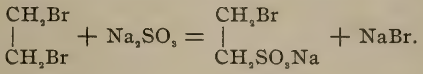
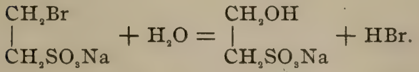
[1] J. Chem. Soc., 9, 250.

[2] Ber. d. chem. Ges., 7, 1163.

[3] J. prakt. Chem., [2] 36, 439.



$$\begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array} + Na_2SO_3 = \begin{array}{l}CH_2Br\\ |\\ CH_2SO_3Na\end{array} + NaBr.$$



$$\begin{array}{l}CH_2Br\\ |\\ CH_2SO_3Na\end{array} + H_2O = \begin{array}{l}CH_2OH\\ |\\ CH_2SO_3Na\end{array} + HBr.$$

The hydrobromic acid liberated then reacts with some of the sulphite present, which accounts for the evolution of sulphur dioxide observed by James.[1] To avoid this secondary reaction the following method of procedure was adopted: Two liters of water, in a three-liter flask supplied with inverted condenser and dropping-funnel, were saturated with sodium sulphite at the boiling-point, and ethylene bromide added through the funnel (as fast as it went into solution) until the odor of sulphur dioxide became perceptible at the mouth of the condenser. The solution was then allowed to cool, when most of the sulphonate formed crystallized out in a practically pure state. After filtration the liquid was heated to boiling, again saturated with sodium sulphite, and ethylene bromide introduced as before. By a repetition of this process about 500 grams of the sulphonate can be obtained from the same liquid, before sodium bromide begins to separate out with the sulphonate. In a trial experiment, 450 grams of ethylene bromide and 1300 grams of sodium sulphite gave 420 grams of pure anhydrous sodium salt—about 95 per cent. of the theoretical yield.

2. *Preparation of the Acid.*—Since the free acid cannot be obtained by decomposing the sulphone chloride the easiest

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[1] J. Chem. Soc., **43**, 44.

way to obtain it, in quantity, is to oxidize ethylene sulphocyanate. This is easily obtained from ethylene bromide by following the directions of Glutz.[1] A much better way of purifying it, however, is to recrystallize it from 1 : 3 nitric acid. After one recrystallization it is obtained in colorless orthorhombic pyramids, which melt sharply at 91° C. If the pure ethylene sulphocyanate thus obtained is warmed with ordinary concentrated nitric acid until vigorous oxidation commences, and the reaction is then allowed to proceed without further heating until gas is no longer evolved, the product, on evaporation, is pure ammonium ethanedisulphonate. If the sulphocyanate is boiled with fuming nitric acid, the product is the free acid. To prepare the latter in a pure condition the sulphocyanate was boiled with fuming nitric acid until a small quantity of the liquid no longer solidified on evaporation, The resulting liquid was diluted with a little water and evaporated to small volume on the water-bath. A dark viscid mass was thus obtained, which solidified almost completely when kept over sulphuric acid for several days. The crystals, when rapidly separated from the liquid, gave reactions for sulphuric and nitric acids. They were therefore dissolved in boiling glacial acetic acid, to which a small quantity of acetic anhydride had been added. This solution, on standing, almost solidified with a mass of slender needles, which melted sharply at 100°. An analysis showed that the substance is pure anhydrous ethanedisulphonic acid :

	Calculated for $C_2H_6S_2O_6$.	Fouud.
C	12.63	12.5
H	3.2	3.3

3. Preparation of the Chloride from the Sodium Salt.—In accordance with the rule given above, the sodium salt of (1, 2)-ethanedisulphonic acid does not react with phosphorus pentachloride in the cold. Even at the temperature of boiling water the reaction is started with difficulty, while above this temperature phosphorus pentachloride readily replaces one of the sulphonic acid groups with chlorine. To prepare large quantities of the chloride the method of procedure was as follows: The sodium salt, dried at 140° and ground to a fine powder, was intimately mixed with a slight excess above the calculated quantity of the pentachloride, and a small quantity of this mixture introduced into a flask and heated over the free flame until reaction commenced; the flask was then transferred to a water-bath, and the rest of the mixture added as fast as liquefaction took place. As soon as the reaction was complete the liquid was poured into a large evaporating dish, and most of the phosphorus oxychloride removed by evaporation on the water-bath. The pasty residue was then allowed to cool, and gradually ground up with ice-water. It was thus obtained as a fine white powder which, after drying on plates, was almost pure, containing only small quantities of unchanged salt and sodium chloride. To get a perfectly pure product it is best to recrystallize from chloroform or carbon tetrachloride with the help of a Soxhlet extraction-apparatus. All the chloride used in the following experiments was purified in this way. From chloroform it crystallizes in large, compact, orthorhombic tables, which melt at 91° C. In a trial experiment 200 grams of sodium salt gave 180 grams of pure chloride instead of 193 grams calculated. The good yield obtained shows that under these conditions but one chloride is formed, while from the close analogy in structure, between (1, 2)-ethanedisulphonic acid, succinic acid, and orthosulphobenzoic acid :

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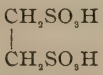
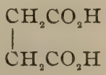
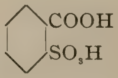
[1] Ann. Chem. (Liebig), 143, 313



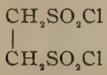
$$\begin{array}{l}\mathrm{CH_2SO_3H}\\ |\\ \mathrm{CH_2SO_3H}\end{array}$$



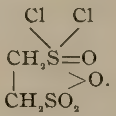
$$\begin{array}{l}\mathrm{CH_2CO_2H}\\ |\\ \mathrm{CH_2CO_2H}\end{array}$$



it seemed probable that the former, like the two latter, would, under suitable conditions, form both a symmetrical and an unsymmetrical chloride :

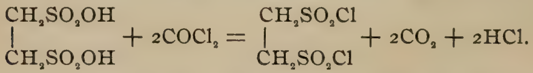


$$\begin{array}{l}\mathrm{CH_2SO_2Cl}\\ |\\ \mathrm{CH_2SO_2Cl}\end{array}$$



To study the influence of temperature the sodium salt was first ground up with phosphorus oxychloride and the pentachloride then added in small portions. Reaction took place in the cold, and the flask was kept in ice-water until the reaction was completed. The solution of the chloride in phosphorus oxychloride was filtered off, and the oxychloride removed at the ordinary temperature, by drawing a rapid current of dry air through it. The same chloride crystallized out. Twenty grams of the sodium salt gave 18.5 grams of pure chloride. The same result was obtained when carbon tetrachloride and carbon bisulphide were used as solvents for the pentachloride.

4. Preparation of the Chloride from the Acid and Carbonyl Chloride.—The free acid behaves towards phosphorus pentachloride exactly like the sodium salt; the chloride melting at 91° C. is obtained in theoretical quantity. To avoid the use of chloride of phosphorus one molecule of the acid was sealed up with slightly more than two molecules of carbonyl chloride in toluene solution, and the two allowed to remain in contact, at the ordinary temperature, until all the acid had gone into solution. The tube, when opened, showed considerable pressure, which was found to be due to carbon dioxide. The contents were allowed to evaporate spontaneously in the air, when the pure chloride, melting at 95°, crystallized out. The reaction is quantitative—20 grams of the acid gave 22.5 grams of the chloride. The only reaction which seems possible under these conditions is represented by the equation :



$$\begin{array}{l} CH_2SO_2OH \\ | \\ CH_2SO_2OH \end{array} + 2COCl_2 = \begin{array}{l} CH_2SO_2Cl \\ | \\ CH_2SO_2Cl \end{array} + 2CO_2 + 2HCl.$$

Hence (1,2)-ethanesulphone chloride must be regarded as symmetrical. As unsymmetrical chlorides are generally obtained through the anhydrides, many unsuccessful efforts were made to obtain an anhydride of the disulphonic acid. The acid loses one of the sulphonic acid residues more readily than it loses a molecule of water.

Chemical Properties of the Chloride.

1. Behavior on Heating.—Heated in quantity in an oil-bath, the chloride begins to sublime perceptibly at about 80°, then melts to a clear colorless liquid at 91°. If the chloride is perfectly pure this liquid can be heated to 150° without a trace of decomposition. At this temperature the chloride sublimes rapidly, the vapor condensing in the form of long slender needles, with the same melting-point as before. At 160° a slow evolution of gas is observed, and if the temperature is kept constant between 160° and 165°, a colorless liquid slowly distils over, while the residue becomes darker in color. The distillation stops when the weight of the distillate is about one-fourth of the original weight of chloride. The gas evolved was found to be sulphur dioxide with a trace of hydrochloric acid. The distillate was submitted to fractional distillation, but it was found impossible to get any fraction boiling at a constant temperature. Hence, all the fractions were combined, and the whole distillate boiled with water in a flask connected with an inverted condenser. Most of it went into solution with evolution of hydrochloric acid. The portion insoluble in water was distilled off with steam. It was found to be a mixture containing carbon, hydrogen, and chlorine, but no sulphur, and it was not further studied. The aqueous solution remaining after distillation with steam was evaporated on the water-bath until free from hydrochloric acid, then neutralized with ammonia, and the product purified by recrystallization from absolute alcohol. Thus purified it was obtained in the form of large, colorless needles, or plates, readily soluble in alcohol and water, and melting at 192°. An analysis of the substance, dried at 120°, gave the following results:

	Calculated for $C_2H_8ClSO_3N$.	Found.	
		I.	II.
C	14.0	14.8	14.7
H	5.1	5.2	5.25
Cl	22.0	22.2	22.18
N	8.73	8.4	8.8

The substance analyzed was the ammonium salt of (1, 2)-chlorethanesulphonic acid. It was compared with a specimen of this salt, obtained by treating isethionic acid with phosphorus pentachloride, and converting the resulting (1, 2)-chlorethanesulphone chloride into the ammonium salt. The two were found identical. A mixture of the two melts sharply at the same temperature at which each melts singly. The distillate, therefore, was composed principally of (1, 2)-chlorethanesulphone chloride.

The residue, after heating, was a tarry mass, which contained both chlorine and sulphur, but no pure substance could be isolated from this. When the chloride is heated, therefore, about 25 per cent. of it is decomposed according to the equation :

$$C_2H_4(SO_2Cl)_2 = CH_2Cl.CH_2SO_2Cl + SO_2.$$

The rest suffers a more complex decomposition, resulting in the formation of halogen substitution-products of the hydrocarbons along with more complicated products.

2. *Action of Water.*—The chloride reacts with water at all temperatures ; both sulphur dioxide and hydrochloric acid can be detected in ice-water that has stood in contact with it for a few minutes. At ordinary temperatures the reaction proceeds very slowly. To follow the reaction quantitatively five portions of one gram each were sealed up with quantities of water varying from 1 to 10 grams, and set aside. The portion which had been sealed up with but one gram of water had not decomposed completely, when the tube was opened, after a lapse of two years. All the remaining portions required from three to four months for complete solution. Two of the tubes were opened under water previously freed from air, and the amount of sulphur dioxide determined by distillation into standard iodine.

I. The sulphur dioxide from one gram of chloride, sealed up with 3 grams of water, reduced 119.3 cc. standard iodine, and, therefore, contained 0.235 gram sulphur dioxide, which is equivalent to 23.5 per cent. of the weight of chloride taken.

II. The sulphur dioxide from one gram chloride sealed up with 10 grams water reduced 116.7 cc. of standard iodine. It, hence, contained 0.23 gram sulphur dioxide, equivalent to 23 per cent. of the weight of chloride.

The two remaining tubes were opened under strongly acid silver nitrate solution, and the hydrochloric acid determined gravimetrically:

III. One gram chloride gave 1.2660 gram silver chloride containing 0.3140 gram chlorine, which is equivalent to 31.4 per cent. of the chloride taken.

IV. One gram chloride gave 1.2640 gram silver chloride containing 0.3134 gram chlorine, equivalent to 31.34 per cent. Calculated for ethanesulphone chloride, 31.27 per cent. chlorine, and 56 per cent. sulphur dioxide.

These results show that when the chloride reacts with cold water all of the chlorine is obtained as hydrochloric acid, while somewhat less than half (41.2 per cent.) of the sulphur is split off as sulphur dioxide.

Boiling water decomposes the chloride much more readily, a steady stream of sulphur dioxide being given off. To isolate the organic products, the resulting liquid was boiled until all the sulphur dioxide had been expelled when evaporated until a few drops of the residue no longer gave a precipitate with silver nitrate. The thick, straw-colored liquid thus obtained was neutralized with an excess of concentrated ammonia, and evaporated to complete dryness. To remove the last traces of water, small quantities of absolute alcohol were added and the evaporation repeated until finally the entire product was obtained in the form of a yellowish powder. This was transferred to a flask connected with an inverted condenser, and boiled with absolute alcohol. Most of the powder dissolved. The residue insoluble in alcohol was easily purified by solution in a small quantity of water and precipitation with alcohol. An analysis of the substance dried at 120° gave the following result:

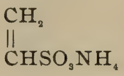
	Calculated for $C_2H_{12}S_2O_6N_2$.	Found. I.	Found. II.
C	10.8	10.46	11.0
H	5.4	5.38	5.45
N	12.5	12.5	12.6

The substance was compared with the ammonium salt of (1, 2)-ethanedisulphonic acid obtained by boiling ethylene bromide with ammonium sulphite, and the two were found the same. 50 grams of the chloride gave 4.2 grams of this salt corresponding to 8.4 per cent, of the chloride. The alcoholic solution, on evaporation, deposited a second ammonium salt, which was purified by several recrystallizations from absolute alcohol. Analysis showed that the substance had the composition of an ammonium salt of ethylenesulphonic acid:

	Calculated for $C_2H_7SO_3N$.	Found. I.	Found. II.
C	19.2	19.05	19.1
H	5.64	5.84	5.4
N	11.2	11.2	11.22
S	25.5	25.5	25.4

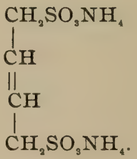
The salt is extremely soluble in water, readily soluble in 95 per cent. alcohol, moderately soluble in absolute alcohol, insoluble in ether. It cannot be crystallized from water. From absolute alcohol it crystallizes in large, thin plates, and from ordinary alcohol in monoclinic tables. Heated rapidly, it melts almost completely at 156°, but solidifies again a few degrees above this point. Like the free acid and all the other salts it instantly reduces alkaline permanganate solution, and reacts with chlorine, bromine, the halogen acids, etc., in the cold. These reactions show that it is a salt of an unsaturated acid. The method of preparation and the analyses permit of but two possibilities:

I.



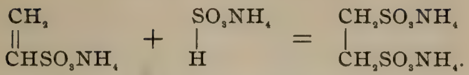
$$\begin{array}{l} CH_2 \\ \| \\ CHSO_3NH_4 \end{array}$$

II.



$$\begin{array}{l} CH_2SO_3NH_4 \\ | \\ CH \\ \| \\ CH \\ | \\ CH_2SO_3NH_4. \end{array}$$

The simplest way to decide between the two is by reduction. The former should give a salt of ethanesulphonic acid, the latter the corresponding salt of (1, 4)-butanedisulphonic acid—both well-known substances. Experiments in this direction, showed, however, that like allyl alcohol and some unsaturated carbonic acids the substance is reduced with great difficulty. A concentrated aqueous solution of the ammonium salt was therefore treated with slightly more than one molecule of acid ammonium sulphite, the solution boiled for a few hours, and allowed to evaporate spontaneously in the air. The characteristic monoclinic prisms of the diammonium salt of (1,2)-ethanedisulphonic acid crystallized out. This could only be formed from a substance having formula I:



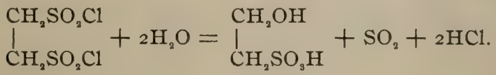
$$\begin{array}{l}CH_2\\ \|\\ CHSO_3NH_4\end{array} + \begin{array}{l}SO_3NH_4\\ |\\ H\end{array} = \begin{array}{l}CH_2SO_3NH_4\\ |\\ CH_2SO_3NH_4.\end{array}$$

50 grams of the chloride gave 24 grams of the ammonium salt, equivalent to 90 per cent. of the chloride.

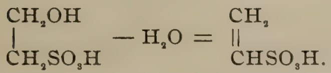
Since the analyses showed that the liquid obtained by the action of water on the chloride, contains all the chlorine in the form of hydrochloric acid and nearly one-half of the sulphur in the form of sulphur dioxide, the ethylenesulphonic acid must have been formed in one of two ways: either the chloride simultaneously loses sulphur dioxide and hydrochloric acid and thus passes directly into the unsaturated acid according to the equation:

$$C_2H_4(SO_2Cl)_2 + H_2O = C_2H_3SO_3H + SO_2 + HCl;$$

or else one of the sulphonic acid groups is first replaced by hydroxyl, and the resulting isethionic acid then loses water during the process of concentrating the acid solution:

I. 

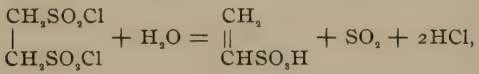
$$\text{I.}\quad \begin{array}{l}CH_2SO_2Cl\\ |\\ CH_2SO_2Cl\end{array} + 2H_2O = \begin{array}{l}CH_2OH\\ |\\ CH_2SO_3H\end{array} + SO_2 + 2HCl.$$

II. 

$$\text{II.}\quad \begin{array}{l}CH_2OH\\ |\\ CH_2SO_3H\end{array} - H_2O = \begin{array}{l}CH_2\\ \|\\ CHSO_3H.\end{array}$$

To determine which of these reactions is true 50 grams of the chloride were decomposed with water, and the product immediately neutralized with lead carbonate. After cooling, the precipitated lead salts were removed by filtration, the lead in solution precipitated with hydrogen sulphide, and the solution of the free acid thus obtained neutralized with ammonia. 50 grams of the chloride gave 23.2 grams of the ammonium salt of the unsaturated acid.

The experiments show that when (1,2)-ethanesulphone chloride is decomposed with hot or cold water about 90 per cent, of it reacts according to the equation:



$$\begin{array}{l}CH_2SO_2Cl\\ |\\ CH_2SO_2Cl\end{array} + H_2O = \begin{array}{l}CH_2\\ \|\\ CHSO_3H\end{array} + SO_2 + 2HCl,$$

while only about 10 per cent. reacts according to the equation:

$$C_2H_4(SO_2Cl)_2 + 2H_2O = C_2H_4(SO_3H)_2 + 2HCl.$$

The quantitative course of the reaction can readily be followed by titrating the sulphur dioxide evolved, with standard iodine.

Many experiments, made with a view of determining the conditions which favor the formation of the unsaturated acid, all led to the conclusion that the action is practically independent of external conditions. It varies only within very narrow limits, and then quite irregularly. The maximum percentage of sulphur dioxide obtained was 25.2; the minimum 20.8.

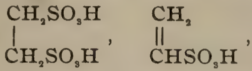
Many transformations of the unsaturated acid have been studied, but for the sake of clearness they will be published in a separate paper.

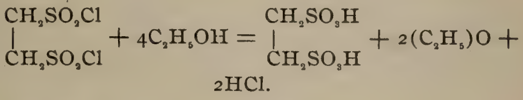
3. Action of Alcohol.—The chlorides dissolve in considerable quantity in cold absolute alcohol. If cold water is added to this solution the chloride is precipitated unchanged. If the solution is allowed to stand, the odor of sulphur dioxide soon becomes perceptible and, after standing for a week, water no longer gives any precipitate. Cold alcohol, therefore, decomposes the chloride much more readily than cold water. The products are easily isolated by distilling off the alcohol, and treating the residue as in previous experiments. The products were found to be the same as those obtained by decomposing the chloride with water, but in quite different quantities:

50 grams of chloride decomposed with cold alcohol gave only 12.2 grams of ammonium ethylenemonosulphonate, corresponding to 45 per cent. of the chloride.

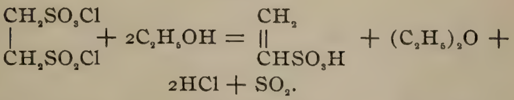
50 grams of chloride, decomposed with boiling alcohol, gave 20 grams of the same salt, corresponding to 60 per cent. of the chloride.

The alcoholic distillate, neutralized with solid soda and submitted to fractional distillation, gave a low-boiling fraction which contained ether, easily recognizable by the odor, and some halogen compound recognized by Beilstein's test. It was heated with an excess of ammonium sulphite in a sealed tube and the product isolated in the usual way. A nitrogen determination showed that ammonium ethanesulphonate had been formed: Found N, 10.92 per cent; calculated for $C_2H_9NSO_3$, N, 11.1 per cent.

The products of the reaction between alcohol and the chloride are therefore  $\begin{array}{l} CH_2SO_3H \\ | \\ CH_2SO_3H \end{array}$, $\begin{array}{l} CH_2 \\ \| \\ CHSO_3H \end{array}$, $(C_2H_5)_2O$, and C_2H_5Cl. Ethyl chloride is probably a secondary product. The main reactions are:

(1) 

$$\begin{array}{l} CH_2SO_2Cl \\ | \\ CH_2SO_2Cl \end{array} + 4C_2H_5OH = \begin{array}{l} CH_2SO_3H \\ | \\ CH_2SO_3H \end{array} + 2(C_2H_5)O + 2HCl.$$

(2) 

$$\begin{array}{l} CH_2SO_3Cl \\ | \\ CH_2SO_2Cl \end{array} + 2C_2H_5OH = \begin{array}{l} CH_2 \\ \| \\ CHSO_3H \end{array} + (C_2H_5)_2O + 2HCl + SO_2.$$

Methyl, propyl, and amyl alcohols react in the same way as ordinary alcohol, but the relative quantities of the two sulphonic acids formed, vary with the different alcohols. Since the presence of the alcohols interferes with the determination of the amount of sulphur dioxide evolved, another method was adopted for following the reaction. In the presence of sodium carbonate, potassium permanganate oxidizes the unsaturated sulphonic acid to sulphuric acid, carbon dioxide, and water. The reaction is quantitative, hence by using standard permanganate the amount of unsaturated acid formed can readily be determined. One-gram portions of the chloride were lowered into a large excess of the boiling alcohol contained in a flask connected with an inverted condenser. After boiling for an hour most of the alcohol was distilled off, the residue neutralized with aqueous sodium carbonate, and the rest of the alcohol completely removed by distillation with steam. The liquid was then cooled and titrated against permanganate, which had been standardized with the sodium salt of the unsaturated acid. The results, expressed in percentages of chloride, are as follows:

	I.	II.	III.	Mean.
Boiling water	88.5	88.0	88.0	88.2
Methyl alcohol	73.0	73.8	73.2	73.3
Ethyl alcohol	60.0	62.0	61.6	61.2
Propyl alcohol	56.8	56.4	56.0	56.4
Amyl alcohol	50.6	50.6	52.0	51.4

As will be seen, the amount of unsaturated acid formed diminishes as the molecular weight of the alcohol increases. This is probably due to the fact that the reaction goes on more slowly in an alcohol of high molecular weight than in an alcohol of low molecular weight. It is independent of the temperature, since the second column of figures was obtained by boiling under an increased pressure of about one atmosphere, the third under diminished pressure.

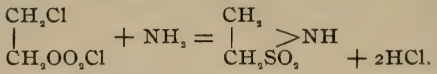
4. Action of Acids and Alkalies.—Glacial acetic acid readily dissolves the chloride; the resulting solution can be boiled for hours without a trace of decomposition. If water is added to the solution, however, decomposition at once sets in, accompanied by evolution of sulphur dioxide. The reaction can be closely followed by the permanganate method, hence it furnishes an easy method for studying the influence of the mass of water, under strictly comparable conditions. The results showed that the course of the decomposition is entirely independent of the relative amounts of chloride and water. Of the two reactions which invariable take place when the chloride is decomposed with water one requires only one-half as much water as the other, but the result was the same whether the water was used in sufficient quantity for the one or in an excess for the other. The minimum amount of chloride transformed into the unsaturated acid was 82 per cent.; the maximum amount was 86 per cent. With aqueous alkalies the general result is the same—the two reactions take place side by side regardless of the nature or concentration of the alkali.

5. Action of Ammonia.—The amide of ethanedisulphonic acid cannot be prepared from the chloride. The products that are invariably obtained when the chloride and ammonia are brought together are ammonium chloride, ammonium sulphite, ammonium ethanedisulphonate, and anhydrotaurine.

These substances are obtained when dry ammonia gas slowly reacts with the dry chloride; when the two are brought together in the presence of water or in solution in ether, alcohol, benzene, or chloroform; and when dry ammonium carbonate is ground up with the dry chloride. The reaction takes place most smoothly in absolute alcoholic solution. When ammonia is passed into an alcoholic solution of the chloride, kept cool with running water, a dense white precipitate immediately begins to form. If this is rapidly filtered off as soon as the reaction is complete, it is entirely free from organic matter and contains only ammonium chloride and ammonium sulphite. On warming the filtrate, ammonium ethanedisulphonate begins to crystallize out mixed with a small quantity of ammonium chloride. It is best to evaporate the liquid to half its volume and then allow it to cool when almost all of the ammonium salts crystallize out. The remainder of the alcohol is then distilled off, the pasty residue diluted with water, and all of the halogen present precipitated by boiling with silver carbonate. The filtrate from this precipitate contains all the anhydrotaurine along with a small quantity of the ammonium salt. To separate the two the solution is evaporated to small volume, and four times the volume of absolute alcohol added. The ammonium salt remains in solution while the anhydro compound is precipitated as an oil. It is extremely difficult to get this substance sufficiently pure for analysis. It separates out of its aqueous solution as a thick oil, which ultimately solidifies to a gelatinous mass without a trace of crystallization. A small quantity was finally obtained in crystalline form by allowing a dilute glacial acetic acid solution to evaporate slowly over potassium hydroxide. Thus prepared, it consisted of small colorless needles, moderately soluble in water, difficultly soluble in glacial acetic acid, insoluble in alcohol and ether. It melts sharply at 88°.

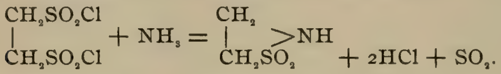
	Calculated for $C_2H_5NSO_3$.	Found. I.	II.
C	24.7	24.5	24.6
H	4.1	4.3	4.28
N	14.4	14.3	14.3
S	35.0	35.1	35.15

The same substance had previously been obtained, in impure condition, by James,[1] by the action of ammonia upon (1, 2)-chlorethanesulphone chloride :



$$\begin{array}{l} CH_2Cl \\ | \\ CH_2OO_2Cl \end{array} + NH_3 = \begin{array}{l} CH_2 \\ | \\ CH_2SO_2 \end{array} \!\! > NH + 2HCl.$$

James gives a different melting-point, but a repetition of his experiment showed that the same substance is formed. The main reaction between ethanedisulphone chloride and ammonia must, therefore, be represented by the equation :

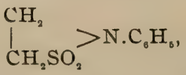


$$\begin{array}{l} CH_2SO_2Cl \\ | \\ CH_2SO_2Cl \end{array} + NH_3 = \begin{array}{l} CH_2 \\ | \\ CH_2SO_2 \end{array} \!\! > NH + 2HCl + SO_2.$$

6. *Action of Aniline.*—When one molecule of the chloride, dissolved in anhydrous ether, is treated with 4 molecules of aniline a reaction takes place in the cold, sulphur dioxide is given off, and the solution almost solidifies with the aniline salts which separate out. After these salts are filtered off the ether still contains two substances in solution. These are most easily separated by repeated extraction with dilute hydrochloric acid. After extraction the ethereal solution is allowed to evaporate spontaneously; when large monoclinic plates separate out. These were dissolved in alcohol, the solution decolorized with bone-black, and evaporated to crystallization. The substance now crystallized out in thick tables melting at 69°. An analysis gave the following results :

	Calculated for $C_8H_9NSO_2$.	Found.	
		I.	II.
C	52.46	52.3	52.2
H	4.9	4.9	5.1
N	7.65	7.6	7.6
S	17.49	17.55	17.6

The substance is anhydrophenyltaurine,



$$\begin{array}{l} CH_2 \\ | \\ CH_2SO_2 \end{array} \!\! > N.C_6H_5,$$

agreeing, in every respect, with the substance obtained by Leymann[2] as one of the products of the action of aniline on

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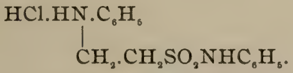
[1] J. prakt. Chem., [2] **20**, 383.

[2] Ber. d. chem. Ges., **18**, 869.

(1, 2)-chlorethanesulphone chloride. From the hydrochloric acid extract a second substance separates out in long needles. This was purified by recrystallization from alcohol containing a small quantity of hydrochloric acid. So purified it forms long colorless needles, which soon become opaque in the air and finally change to a black resinous mass. It is extremely soluble in water, moderately soluble in alcohol, insoluble in ether, and melts at 171°.

	Calculated for $C_{14}H_{17}N_2SO_2Cl$.	Found. I.	II.
C	53.8	53.6	53.5
H	5.44	5.64	5.5
S	10.24	10.24	10.4
Cl	11.4	11.5	11.5
N	8.5	8.5	8.5

The substance is the hydrochloric acid salt of anilidoethanesulphone anilide,



$$\begin{array}{l} HCl.HN.C_6H_5 \\ \quad\quad | \\ \quad\quad CH_2.CH_2SO_2NHC_6H_5. \end{array}$$

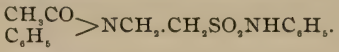
By decomposing the salt with the calculated quantity of an alkali, the free base is obtained as an oil, which is difficult to obtain in crystalline form. It is insoluble in water but, by reason of the two differently located aniline residues, soluble both in alkalies and acids. If ammonium chloride solution is allowed to diffuse slowly into the solution in dilute caustic potash the base separates out in colorless plates melting at 75°.

	Calculated for $C_{14}H_{17}N_2SO_2$.	Found. I.	II.
C	66.5	66.3	66.35
H	6.1	5.8	5.9
N	10.1	10.3	10.3

The base is most easily identified in the form of its monoacetyl derivative, which is formed when it is boiled for a short time with acetyl chloride or acetic anhydride. It is readily soluble in alcohol and ether, difficultly soluble in water, and melts at 152°.

	Calculated for $C_{16}H_{19}N_2SO_3$.	Found. I.	II.
N	8.8	8.8	8.9

Since the acetyl derivative is still soluble in alkalies it must be acetylphenylamidoethanesulphone anilide

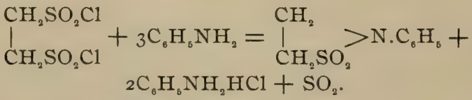


$$\begin{matrix}CH_3CO\\C_6H_5\end{matrix}\!>\!NCH_2.CH_2SO_2NHC_6H_5.$$

The mixture of salts insoluble in ether can be separated by recrystallization from absolute alcohol. One is aniline hydrochlorate melting at 192°. The other is the aniline salt of ethanedisulphonic acid, readily soluble in water and alcohol, insoluble in ether. From alcohol it crystallizes in colorless plates which do not melt without decomposition.

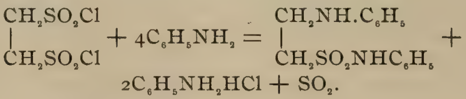
	Calculated for $C_{14}H_{20}N_2S_2O_6$.	Found. I.	Found. II.
N	7.4	7.6	7.45

These same products are obtained when aniline acts upon the chloride under any other conditions, although the relative quantities vary. If aniline is allowed to drop into the molten chloride the main reaction is



$$\begin{matrix}CH_2SO_2Cl\\|\\CH_2SO_2Cl\end{matrix} + 3C_6H_5NH_2 = \begin{matrix}CH_2\\|\\CH_2SO_2\end{matrix}\!>\!N.C_6H_5 + 2C_6H_5NH_2HCl + SO_2.$$

In the presence of solvents the main reaction is



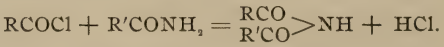
$$\begin{matrix}CH_2SO_2Cl\\|\\CH_2SO_2Cl\end{matrix} + 4C_6H_5NH_2 = \begin{matrix}CH_2NH.C_6H_5\\|\\CH_2SO_2NHC_6H_5\end{matrix} + 2C_6H_5NH_2HCl + SO_2.$$

In the presence of water a considerable quantity of the aniline salt of ethanedisulphonic acid is formed.

Reaction with Acid Amides.—It has been shown, by a number of different investigations, that acid chlorides generally react with acid amides in one of three ways, *viz.:*

(1) $RCOCl + R'CONH_2 = RCOOH + R'CN + HCl.$

(2) $RCOCl + R'CONH_2 = RCONH_2 + R'COCl.$

(3) 

$$RCOCl + R'CONH_2 = \begin{matrix}RCO\\R'CO\end{matrix}\!>\!NH + HCl.$$

Since the amide of ethanedisulphonic acid could not be prepared by the usual reactions, an effort was made to prepare it indirectly by realizing the second reaction. A number of different amides were tried, but since the results were essentially the same in all cases only the experiments with acetamide will be described.

One molecule of the chloride and four molecules of acetamide were brought together in glacial acetic acid. Reaction began at once, accompanied by a slow evolution of sulphur dioxide. To complete the reaction, however, it was necessary to warm on the water-bath. After the sulphur dioxide ceased to come off, the acetic acid was removed by distillation, under diminished pressure, and subjected to fractional distillation. A fraction boiling below 90° was neutralized with sodium carbonate, extracted with ether, and again fractioned. This gave a liquid with a constant boiling-point of 81°, found to be pure acetonitrile by saponification to acetic acid. If the distillate was allowed to stand without fractioning the long spear-shaped crystals, characteristic of the hydrochloride of acetamide, $(CH_3CONH_2)_2.HCl$, separated out.

The residue left after removal of the acetic acid was boiled with absolute alcohol. A residue was pure ammonium ethanedisulphonate :

	Calculated for $C_2H_4(SO_3NH_4)_2$.	Found. I.	II.
N	12.8	12.8	12.75

The alcoholic extract contained a considerable quantity of the same salt mixed with another ammonium salt. After repeated recrystallizations from alcohol this was obtained in the form of large monoclinic plates, readily soluble in alcohol and melting at 192°.

Analysis showed that the substance is ammonium chlorethanesulphonate.

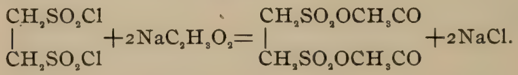
	Calculated for $C_2H_8ClNSO_3$.	Found. I.	II.
C	14.9	14.6	14.75
H	5.1	5.4	5.35
Cl	22.0	22.15	22.1
N	8.7	8.7	8.75
S	19.8	19.75	19.7

It is difficult to account for the formation of such a substance, from a symmetrical chloride. It was, however, repeatedly obtained from the pure chloride, and there can be no doubt as to its structure, since it gives sodium ethanedisulphonate when boiled with sodium sulphite.

7. *Reaction of the Chloride with Salts of Organic Acids.*—When the chloride is brought in contact with a salt of some organic acid in the presence of a neutral solvent, a peculiar reaction takes place, which illustrates the ease with which this substance passes into an unsaturated acid. If, for instance, a cold solution of one molecule of the chloride in glacial acetic acid is poured into a solution of four molecules of sodium acetate in the same solvent, a rapid evolution of sulphur dioxide commences in the cold, and all the chlorine is precipitated out as sodium chloride. If the acetic acid is distilled off, and the residue purified by recrystallization from alcohol it is found to consist of sodium ethanedisulphonate and the sodium salt of ethylenesulphonic acid. The latter crystallizes from alcohol in long, thin plates, readily soluble in water, difficultly soluble in 95 per cent. alcohol, insoluble in absolute alcohol. It instantly reduces permanganate and decolorizes bromine water in the cold. Analysis gave the following results :

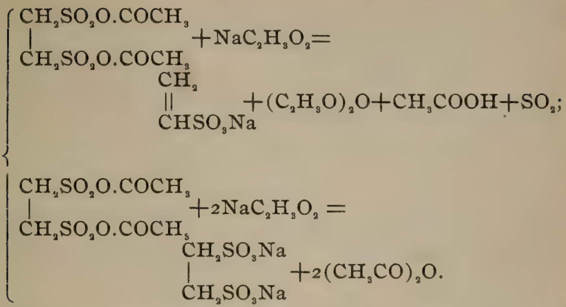
	Calculated for $C_2H_3SO_3Na$.	Found. I.	II.
C	18.6	18.45	18.4
H	2.3	2.5	2.55
Na	17.7	17.7	17.82

The distillate, on fractioning, gave a portion which boiled considerably above the boiling-point of acetic acid, and hence must have contained acetic anhydride. The reaction probably takes place in several stages :

1. 

$$\begin{array}{l} CH_2SO_2Cl \\ | \\ CH_2SO_2Cl \end{array} + 2NaC_2H_3O_2 = \begin{array}{l} CH_2SO_2OCH_3CO \\ | \\ CH_2SO_2OCH_3CO \end{array} + 2NaCl.$$

2.



$$2.\ \begin{cases} \begin{matrix}CH_2SO_2O.COCH_3\\ | \\ CH_2SO_2O.COCH_3\end{matrix} + NaC_2H_3O_2 = \begin{matrix}CH_2\\ \| \\ CHSO_3Na\end{matrix} + (C_2H_3O)_2O + CH_3COOH + SO_2; \\ \\ \begin{matrix}CH_2SO_2O.COCH_3\\ | \\ CH_2SO_2O.COCH_3\end{matrix} + 2NaC_2H_3O_2 = \begin{matrix}CH_2SO_3Na\\ | \\ CH_2SO_3Na\end{matrix} + 2(CH_3CO)_2O. \end{cases}$$

About 95 per cent. of the chloride used passes into a salt of the unsaturated acid, if acetic acid is used as the solvent. The reaction also takes place when alcohol is used as the solvent, but the amount of unsaturated acid obtained is considerably less. Any organic salt soluble in alcohol may be substituted for the acetate. If a difficultly soluble salt like ammonium oxalate is mixed with the chloride and a small quantity of alcohol added, the salt and the chloride go into solution and oxalic acid and ammonium chloride crystallize out.

8. *The Action of Zinc Dust.*—The action of zinc dust was studied by Otto and Casanova,[1] who obtained the zinc salt of (1,2)-ethanedisulphinic acid. As they do not state what yield of sulphinic acid was obtained, or whether any other substances are formed, their experiments were repeated. The chloride was treated with zinc dust according to the directions of Otto and Schiller,[2] the mixture being kept cool with running water. After the zinc chloride had been removed with cold water, the residue was digested with sodium carbonate, filtered and evaporated to small volume. It was then treated with aqueous alcohol which precipitated a considerable quantity of a sodium salt free from organic matter. This was found to consist mainly of sodium sulphite and sodium sulphate mixed with a small quantity of sodium carbonate. From the alcoholic solution the sodium sulphinate was obtained with the properties described by Otto. The maximum yield corresponded to 53 per cent. of the chloride. The small yield

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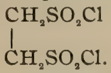
[1] J. prakt. Chem., [2] **26**, 439.

[2] Ber. d. chem. Ges., **9**, 1585.

and the formation of sodium sulphite and sodium sulphate show that a considerable quantity of the chloride reacts in a different way. The greater part of the product of this second reaction is found with the zinc chloride in the aqueous solution. As the study of this substance is still being carried on, its description will be reserved for a subsequent paper.

Summary.

I. (1, 2)-Ethanedisulphonic acid forms but one chloride which is probably symmetrical (1, 2)-ethanedisulphone chloride,



$$\begin{array}{l} CH_2SO_2Cl \\ | \\ CH_2SO_2Cl. \end{array}$$

II. (1, 2)-Ethanedisulphone chloride is stable to 160°. Above this temperature it is decomposed according to the equation: $C_2H_4(SO_2Cl)_2 = CH_2Cl.CH_2SO_2Cl + SO_2$.

III. Whenever any substance acts upon the chloride two reactions take place. The main reaction results in the formation of the lowest member of the unsaturated sulphonic acid series, $CH_2{=}CHSO_3H$, some derivative of this acid, or a derivative of ethanemonosulphonic acid. A subordinate reaction results in the regeneration of (1, 2)-ethanedisulphonic acid.

IV. When water, alcohol, and other hydroxyl compounds act upon the chloride the main product is ethylenesulphonic acid or one of its derivatives.

V. When ammonia or substituted ammonias react with the chloride a substitution-product of ethanesulphonic acid forms the main product.

VI. When acid amides react with the chloride the main product is a derivative of (1,2)-chlorethanesulphonic acid.

VII. The best way to prepare unsaturated sulphonic acids is to decompose with water the chlorides of polysulphonic acids, which have sulphonic acid residues in the 1, 2 positions with reference to each other.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE.

THE DISSOCIATION OF ELECTROLYTES AS MEASURED BY THE BOILING-POINT METHOD.

BY HARRY C. JONES AND STEPHEN H. KING.

The two methods of general application for measuring the amount of electrolytic dissociation in aqueous solutions, are, the conductivity method of Kohlrausch,[1] and the freezing-point method of Beckmann in its most improved forms.[2] There are, in addition, several methods available for determining the concentration of particular kinds of ions, or which admit of application to a limited number of cases, as the well-known solubility method of Nernst and Noyes.[3] The two methods which can be used satisfactorily with water solutions are, in turn, of limited applicability when other solvents are employed. The use of conductivity as a direct measure of dissociation is most satisfactory when water is used as a solvent. A difficulty which is encountered with other solvents is, that the dissociation in them is not complete at dilutions which come within the range of that method. The value of $M\infty$ cannot, therefore, be determined directly, and some assumption, which may require proof, is sometimes made in an attempt to determine its approximate value. Considerable work has, however, already been done on the conductivity of solutions of electrolytes of different concentrations in solvents other than water; notably the work of Fitzpatrick,[2] Paschkow,[2] and Völlmer,[3] on solutions in ethyl and methyl alcohol; of Zelinsky and Krapiwin[4] on solutions in methyl alcohol; and of Zanninovich-Tessarin[5] on solutions in formic acid.

The freezing-point method can also be successfully applied to only a limited number of solvents, and especially well only to water solutions. It may, perhaps, be applicable to solutions in benzene, acetic acid, and other solvents whose freezing points are not widely removed from the ordinary temperature. But many solvents do not come within its range because their points of solidification lie too low to enable one to apply the freezing-point method with even a fair degree of accuracy. For such solvents it seems that the boiling-point method is the only one available, and this only when it has been worked out with sufficient accuracy to enable one to place a fair amount of confidence in the results. On the other hand, the boiling-point method is not easily applied to water solutions, owing in part to the very small value of the constant for that solvent.

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[1] Ann. der Phys., Wied., **26**, 161.

[2] *Ibid*, **51**, 500; Ztschr. phys. Chem., **11**, 529.

[3] Ztschr. phys. Chem., **4**, 372; **6**, 241.

[4] Phil. Mag., 377 (1887).

[5] Uber die Leitfähigkeit einiger Salze in alkohol Lösungen. Charkow. 1892.

[6] Ann. der Phys. Wied., **52**, 328.

[7] Ztschr. phys. Chem., **21**, 35.

[8] *Ibid*, **19**, 251.

One of the causes why the physical chemistry of to-day is primarily the physical chemistry of water solutions, is doubtless the greater dissociating action of that solvent. But another, which is strongly operative, is the absence of a reliable method with which to measure accurately the amount of dissociation in other solvents. This alone would show the importance attached to such determinations.

The interest in such measurements is, however, still further increased by the relation between the dielectric constants of solvents and their dissociating power, which has been pointed out on theoretical grounds for the first time in a readily accessible scientific journal, by J. J. Thomson,[1] and about the same time by W. Nernst.[2] Whether such a relation exists rigidly and quantitatively,—whether dissociating power is a function of any one physical property of the solvent, can be determined only by a careful study of the dissociation of electrolytes in the different solvents in question. In order that such work may be done, it is necessary that a method be worked out which will meet the requirements of practicability and accuracy.

The object of this preliminary notice is to call attention to the fact that we have such, in an improved form of the Beckmann boiling-point method, which he devised for the determination of the molecular weights of non-electrolytes. The essential feature in the new boiling-point apparatus[3] is the introduction of a platinum cylinder around the thermometer, which cuts off the effect of radiation, and at the same time prevents the condensed solvent from coming in contact with the thermometer until it has been reheated. The determinations of the molecular weights of a number of non-electrolytes in five solvents, whose boiling-points vary from 35° to 182°, show that we have to deal with the simplest efficient boiling-point apparatus thus far constructed. We have already applied it to the measurement of the electrolytic dissociation of solutions of two electrolytes, potassium iodide and sodium acetate, in ethyl alcohol, and the results will show the degree of accuracy of which the method is capable.

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[1] Phil. Mag., **36**, 320.

[2] Göttinger Nachrichten, 1893: and Ztschr. phys. Chem., **13**, 531.

[3] This JOURNAL, **19**, 581.

The reason why the boiling-point method has not already found extensive application in measuring dissociation is, doubtless, to be sought in the fact that it has not been worked out with accuracy sufficient to enable it to be applied with a fair degree of probability.

The alcohol used in this work was dehydrated in the usual manner. It was allowed to stand for some days over quicklime, distilled and preserved in contact with anhydrous copper sulphate. The sodium acetate used was prepared by dissolving metallic sodium in water, neutralizing the sodium hydroxide formed with acetic acid, evaporating the solution of sodium acetate to dryness, and finally drying in an air-bath, above 100°, to constant weight. The results given below are distinctly tentative and solutions of both of the compounds in question will be worked over in the future with still greater care than has been possible thus far. The prime object in publishing these values at present is to show the fair agreement between the dissociation values as determined for the same substances, under the same conditions.

The Results.

SOLVENT, ALCOHOL. Molecular rise in 100 grams 11.5°.

Potassium Iodide, molecular weight 166.

Grams solvent.	Grams potassium iodide.	Grams iodide to 100 grams solvent.	Rise in boiling-point.	Molecular rise.	Dissociation. Per cent.
53.553	1.6470	3.076	0.271°	14.625	27.2
56.234	1.2945	2.302	0.200	14.419	25.4
54.533	1.080	1.9804	0.172	14.417	25.4
58.572	1.389	2.371	0.208	14.566	26.7
58.900	1.060	1.800	0.158	14.576	26.7

Sodium Acetate, molecular weight 82.1.

Grams solvent.	Grams sodium acetate.	Grams acetate in 100 grams solvent.	Rise in boiling-point.	Molecular rise.	Dissociation. Per cent.
57.599	0.747	1.2969	0.185°	11.711	1.8
57.599	1.217	2.1129	0.299	11.616	1.0
57.878	0.5997	1.0361	0.147	11.648	1.3
57.878	0.9715	1.6785	0.238	11.640	1.2

In these determinations the barometer was read every few minutes and the boiling points were corrected for any change in atmospheric pressure, however slight. While very small changes in the barometer can be neglected when the question under investigation is one of molecular weights, they must always be carefully taken into account when far more accurate measurements are necessary, as in the case of the measurement of dissociation.

It will be seen from the results that the dissociation of potassium iodide in alcohol is between one-third and one-fourth of that in water at the same dilution. This is just about the same ratio as exists between the dielectric constants of these two solvents.

The dissociation found for sodium acetate in alcohol is almost certainly too low. Indeed the metallic sodium used in preparing the hydroxide was found to contain more than a trace of potassium, and this may account in part for the very low values.

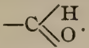
We propose to extend the application of this method to a large number of electrolytes, and to as many solvents as may be practicable.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
June, 1897.

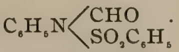
Contributions from the Sheffield Laboratory of Yale University.

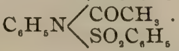
LIV.—ON DIACYL ANILIDES.

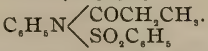
BY H. L. WHEELER, T. E. SMITH, AND C. H. WARREN.

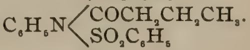
It has frequently been observed that formanilide shows a departure from the other anilides in many of its properties, and it has been stated that this would seem to indicate that it is not an anilide or, in other words, that it does not contain the formyl group  $—C{<}\begin{matrix}H\\O\end{matrix}$.

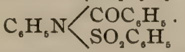
In the diacyl anilides the formyl group exists as represented above, and it seemed of interest to compare crystallographically the formyl derivative in one of these series with those of its homologues. We have, therefore, prepared the following series of diacyl anilides, and find that some of these compounds are especially suitable for a crystallographic examination:

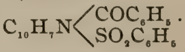
Formylbenzenesulphanilide,  $C_6H_5N{<}\begin{matrix}CHO\\SO_2C_6H_5\end{matrix}$.

Acetylbenzenesulphanilide,  $C_6H_5N{<}\begin{matrix}COCH_3\\SO_2C_6H_5\end{matrix}$.

Propionylbenzenesulphanilide,  $C_6H_5N{<}\begin{matrix}COCH_2CH_3\\SO_2C_6H_5\end{matrix}$.

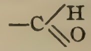
n-Butyrylbenzenesulphanilide,  $C_6H_5N{<}\begin{matrix}COCH_2CH_2CH_3\\SO_2C_6H_5\end{matrix}$.

Benzoylbenzenesulphanilide,  $C_6H_5N{<}\begin{matrix}COC_6H_5\\SO_2C_6H_5\end{matrix}$.

Benzoylbenzenesulph-α-naphthalide,
Benzoylbenzenesulph-β-naphthalide,  $C_{10}H_7N{<}\begin{matrix}COC_6H_5\\SO_2C_6H_5\end{matrix}$.

The results of the crystallographic examination of these compounds show that acetyl and propionylbenzenesulphanilide exhibit close crystallographic analogy, the compounds being monoclinic, hemimorphic, and pyroelectric, their crystallographic axes and the angle β being similar.

On the other hand, formylbenzenesulphanilide, which is orthorhombic, shows no analogy whatever with these compounds. It may be added that crystals of formanilide which we obtained show no analogy with those of acetanilide.

Since a compound with the true formyl group may exhibit a departure in physical properties from those of the homologues it follows that a similar departure in physical properties in the case of formanilide, formic acid,[1] etc., cannot be taken as evidence against the presence of the group  $-C{\diagup H \atop \diagdown O}$ in these compounds.

Knight[2] has recently investigated the action of benzoyl chloride on benzenesulphanilide on the one hand, and of benzenesulphochloride on benzanilide on the other, with the expectation of obtaining benzoylbenzenesulphanilide if benzanilide has the normal structure. As a matter of fact, the reactions did not proceed as expected, but in both cases dibenzanilide was formed.

Believing this result to be due to the secondary action of hydrogen chloride, which is formed in both reactions, we have heated benzoylbenzenesulphanilide with dry hydrogen chloride, and have found that benzoyl chloride was liberated, and also that the diacylanilide, in the presence of benzoyl chloride, is readily converted into dibenzanilide.

The explanation of the formation of dibenzanilide in the case of Knight's experiment is therefore as follows: Benzoylbenzenesulphanilide is first formed in both cases, and a portion of this in the presence of the resulting hydrogen chloride forms benzoyl chloride, which converts the remaining benzoylbenzenesulphanilide into dibenzanilide. This is the more probable, since Knight states that in both cases the same phenomena were observed. Moreover, it has been customary to prepare diacylsulphamides by heating the sulphamides with acyl chlorides. These results are, therefore, in favor of the normal structure for benzanilide.

The diacylanilides containing the benzenesulpho groups behave with alkali precisely like the other mixed diacylanilides. In each case, so far as examined, the lower acyl group is first removed.[3]

The authors take pleasure in acknowledging their great indebtedness to Professor S. L. Penfield, under whose direction the following crystallographic results were obtained:

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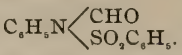
[1] Freer and Sherman: This JOURNAL, 18, 526.

[2] This JOURNAL, 19, 152.

[3] Compare also Remsen and Palmer: This JOURNAL, 8, 243.

Experimental Part.

Formylbenzenesulphanilide, 
$C_6H_5N\langle\begin{smallmatrix}CHO\\SO_2C_6H_5\end{smallmatrix}$.—This compound was prepared by acting on phenylformimidoethyl ester with benzenesulphochloride, as previously described.[1] The structure assigned to this substance follows from its method of preparation and its subsequent decomposition with alkali. The crystals for measurement were obtained from absolute alcohol in each case. Formylbenzenesulphanilide is orthorhombic, and the following forms were observed:

a, 100	*m*, 110	*e*, 201
b, 010	*d*, 101	*p*, 111

The measurements are as follows, those marked with an asterisk being taken as fundamentals.

			Measured.	Calculated.
a ∧ *e*,	100 ∧ 201	=	55° 53′*	
a ∧ *d*,	100 ∧ 101	=	71 15	71 17′
m ∧ *m*,	110 ∧ $1\bar{1}0$	=	67 44*	
d ∧ *d*,	101 ∧ $\bar{1}01$	=	37 25	37 25
p ∧ *d*,	111 ∧ 101	=	23 17	23 18
p ∧ *a*,	111 ∧ 100	=	72 51	72 50
p ∧ *p*,	111 ∧ $\bar{1}11$	=	34 14	34 18
b ∧ p,	010 ∧ 111	=	66 39	66 42

axes $a : b : c = 0.6711 : 1 : 1.0993$.

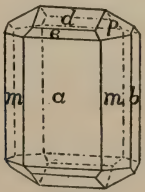
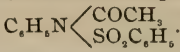


Fig. 1.

The crystals of formylbenzenesulphanilide present the habit shown in Fig. 1. They were small when compared with some of the other diacyl anilides, rarely exceeding 5 mm. in length. They have a tendency to grow in the direction of

[1] Wheeler and Walden: This JOURNAL, 19, 135.

the ċ axis. On the majority of the crystals it was found that the full number of the *e* and *d* faces were not developed, thus giving the crystals a decidedly monoclinic aspect.

Acetylbenzenesulphanilide,  $C_6H_5N\langle^{COCH_3}_{SO_2C_6H_5}$.—This and the following diacyl anilides were prepared by acting on the sodium salts of the sulphanilide in dry benzene with acid anhydrides. Their formation results more smoothly in this manner than when the sulphanilides are heated with acid chlorides. The structure assigned to these substances follows from their method of preparation, since Blacher[1] has shown that the sodium salt of benzamide gives with benzoic and acetic anhydrides dibenzamide and acetbenzamide, and these diacylamides have both acyl groups attached to nitrogen, as proved conclusively by Wheeler and Walden.[2]

Acetylbenzenesulphanilide separates from very dilute solutions in the form of large, rough, colorless, monoclinic plates, having a tendency to form clusters. From more concentrated solutions small, finely developed crystals, 1 to 2 mm. in length grow, while from still more concentrated solutions the substance comes down in long thin needles. When the material was crystallized from alcohol it melted constantly at 116°.5. A nitrogen determination gave the following result :

	Calculated for $C_{14}H_{13}NO_3S$.	Found.
N	5.09	4.91

The crystals are hemimorphic, as shown in Fig. 2. The forms observed are :

a, 100	*s*, $\bar{1}01$	*p*, $\bar{1}11$
b, 010	*d*, 011	
c, 001	d_1, $0\bar{1}1$	

The faces *b*, *d*, and *p* were observed at that extremity of the *b* axis, where negative electricity developed, when the crystals, which had been heated for some time, were cooled, while at the other extremity *d* alone occurred.

The measurements obtained are as follows :

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[1] Ber. d. chem. Ges., **28**, 2356.

[2] *Loc. cit.*

			Measured.	Calculated.
$a \wedge c$,	$100 \wedge 001$	=	64° 56′*	
$d \wedge d$,	$011 \wedge 01\bar{1}$	=	75 59*	
$c \wedge s$,	$001 \wedge \bar{1}01$	=	63 56*	
$c \wedge d$,	$001 \wedge 011$	=	51 59	52° 0½′
$a \wedge d$,	$100 \wedge 011$	=	75 0	74 52
$a \wedge p$,	$\bar{1}00 \wedge \bar{1}11$	=	64 52	65 2
$p \wedge d$,	$\bar{1}11 \wedge 011$	=	40 8	40 6
$s \wedge p$,	$\bar{1}01 \wedge \bar{1}11$	=	47 44	
$p \wedge d$,	$11\bar{1} \wedge 011$	=	84 48	84 49

Axes = $a:b:c$ = 1.225 : 1 : 1.4138. β = 100 ∧ 001 ∧ 64°-59°.

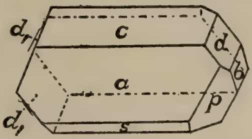
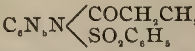


Fig. 2.



Propionylbenzenesulphanilide, $C_6N_5N\left\langle\begin{matrix}COCH_2CH_3\\SO_2C_6H_5\end{matrix}\right.$.—The product of the action of propionic anhydrid on sodium benzenesulphanilide was crystallized from absolute alcohol when it melted constantly at 115°.

	Calculated for $C_{15}H_{15}NO_3S$.	Found.
N	4.8	4.7

The crystals are hemimorphic, Fig. 3, representing the prevailing habit, while more complicated crystals, like Fig. 4, were only occasionally found.

The forms observed are:

a, 100
b, 010
b_1, $0\bar{1}0$
c, 001
n, $3\bar{1}0$
d, 012
d_1, $0\bar{1}2$
x, $31\bar{2}$
x_1, $3\bar{1}\bar{2}$

The faces x_1 and n_1 are developed at that extremity of the b axis, where positive electricity occurs, when the crystals which had been heated for some time were cooled. The face

x, when observed, was always smaller than x_1, while b and d were about equal in size to b_1 and d_1.

The measurements are as follows :

		Measured.		Calculated.	
$a \wedge d$, $100 \wedge 012$	=	69°	7'*		
$d \wedge d$, $012 \wedge 0\bar{1}2$	=	64	46*		
$a \wedge x$, $100 \wedge 31\bar{2}$	=	38	59*		
$a \wedge c$, $100 \wedge 001$	=	65	0	65°	2'
$b \wedge x$, $010 \wedge 31\bar{2}$	=	68	52	68	52
$a \wedge n_1$, $100 \wedge 3\bar{1}0$	=	19	33	19	31
$c \wedge x$, $00\bar{1} \wedge 31\bar{2}$	=	82	0	82	0
$c \wedge n_1$, $001 \wedge \bar{3}10$	=	66	32	66	33
$b \wedge n_1$, $010 \wedge 3\bar{1}0$	=	70	27	70	29
$d \wedge x_1$, $0\bar{1}\bar{2} \wedge 3\bar{1}\bar{2}$	=	71	54	71	55

Axes $= a : b : c = 1.170 : 1 : 1.390$. $\beta = 100 \wedge 001 = 65° 2'$.

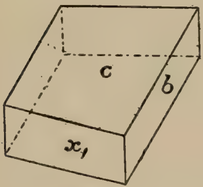


Fig. 3.

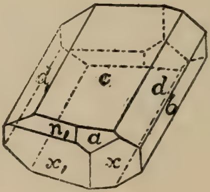
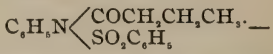


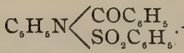
Fig. 4.

From very dilute solutions, containing only a few grams of material, this compound grows in crystals enormously elongated in the direction of the a axis, some of the crystals attaining a length of 75 mm. and a diameter of from 2 to 3 mm. On account of the fact that these crystals show entirely different habits from those of the acetyl compounds, it was thought at first that no analogy in crystalline structure existed between them. By adopting, however, appropriate indices for the faces, a close similarity in the axial ratios of these hemimorphic compounds may be observed as follows :

Acetyl $a : b : c = 1.225 : 1 : 1.4138$. $\beta = 64° 56'$.
Propionyl $a : b : c = 1.170 : 1 : 1.390$. $\beta = 65° 2'$.

n-Butyrylbenzenesulphanilide, 
$C_6H_5N\begin{cases}COCH_2CH_2CH_3\\SO_2C_6H_5\end{cases}$.—This compound, prepared in the same manner as the acetyl and propionyl compounds, gave stout prisms when crystallized from alcohol, melting at 89°–90°. Satisfactory measurements, for a crystallographic description, were not obtained. A nitrogen determination gave :

	Calculated for $C_{16}H_{17}NO_3S$.	Found.
N	4.62	4.38

Benzoylbenzenesulphanilide, 
$C_6H_5N\begin{cases}COC_6H_5\\SO_2C_6H_5\end{cases}$.—The crystals of this compound were small and well developed when grown from a dilute solution, not being more than 2 mm. in length. From more concentrated solutions it comes down in long, thin needles. It was found that the crystals of this compound were monoclinic but showed no hemimorphic or pyroelectric properties. When crystallized repeatedly from alcohol they melt from 114°–115°, and a nitrogen determination gave the following results :

	Calculated for $C_{19}H_{15}NO_3S$.	Found.
N	4.15	4.29

The forms observed are :

b, 010 c, 001 m, 110 l, 120 x, $\bar{1}01$

The measurements obtained are the following :

	Measured.	Calculated.
$c \wedge x$, $001 \wedge \bar{1}01$ =	80° 18′*	
$c \wedge m$, $001 \wedge 110$ =	61 50 *	
$m \wedge m$, $1\bar{1}0 \wedge 110$ =	68 56 *	
$m \wedge l$, $110 \wedge 120$ =	19 26	19° 27′
$c \wedge l$, $001 \wedge 120$ =	70 19	70 17
$m \wedge x$, $110 \wedge 10\bar{1}$ =	54 3	54 5
$l \wedge x$, $120 \wedge 10\bar{1}$ =	64 34	65 0

Axes $a : b : c = 0.8373 : 1 : 1.175$. $\beta = 100 \wedge 001 = 55° 4'$.

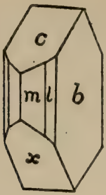


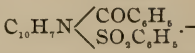
Fig. 5.

Figure 5 represents the prevailing habit of benzoylbenzenesulphanilide. No close crystallographic relation was found between this compound and the preceding ones.

A small quantity of the above compound was heated in a test-tube to 180°. Dry hydrogen chloride was passed in and benzoyl chloride was formed. When the diacylanilide was heated with benzoyl chloride to 180° for ten hours a reddish oil was obtained, which solidified on cooling. This was crystallized from alcohol when a mass of colorless needles was obtained, melting from 160°–161°. A nitrogen determination gave 4.93 per cent. of nitrogen, while the calculated percentages for benzanilide and dibenzanilide are 7.07 and 4.65, respectively. The material formed by this treatment was therefore dibenzanilide.

Benzenesulph-α-naphthalide, $C_{10}H_7NHSO_2C_6H_5$.—This was obtained by the Baumann-Schotten reaction in the usual manner. When crystallized from alcohol it separated in needles and melted from 168°–169°. A nitrogen determination gave :

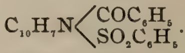
	Calculated for $C_{16}H_{13}NO_2S$.	Found.
N	4.94	4.47

Benzoylbenzenesulph-α-naphthalide, 
$C_{10}H_7N\begin{cases}COC_6H_5\\SO_2C_6H_5\end{cases}$.—
The crude material in this case was purified by boiling with absolute alcohol, washing with sodium hydrate, and then crystallizing from a mixture of benzene and ligroïn. It formed minute crystals, which melted constantly at 193°–194°, and which seemed to be pure. Nitrogen determinations in different samples, however, invariably came low.

	Calculated for $C_{23}H_{17}NO_3S$.	Found.			
		I.	II.	III.	IV.
N	3.61	2.78	3.05	2.72	2.90

Benzenesulph-β-naphthalide, $C_{10}H_7NHSO_2C_6H_5$.—This material crystallized poorly from dilute alcohol in small, oblong plates or flattened prisms, which apparently melted constantly at 97°.

	Calculated for $C_{16}H_{13}NO_2S$.	Found.
N	4.9	4.7

Benzoylbenzenesulph-β-naphthalide, 
$C_{10}H_7N{<}\begin{matrix}COC_6H_5\\SO_2C_6H_5\end{matrix}$.—This consisted of minute, fine, white needles, melting from 161°–162°.

	Calculated for $C_{23}H_{17}NO_3S$.	Found.
N	3.6	3.4

Formanilide, C_6H_5NHCHO.—The crystals for examination in this case were prepared by spontaneous evaporation of a solution of the anilide in a mixture of low-boiling ligroïn and ether. This gave monoclinic crystals about 6 or 7 mm. in length, and the following forms were observed:

a, 100 *c*, 001 *e*, 101 *d*, 011 *p*, 112

The measurements obtained were as follows:

		Measured.	Calculated.
$c \wedge e$, $001 \wedge 101$	=	26° 17′*	
$a \wedge c$, $100 \wedge 001$	=	85 6*	
$c \wedge d$, $001 \wedge 011$	=	67 20	
$a \wedge e$, $100 \wedge 101$	=	58 52	58° 49′
$d \wedge d$, $011 \wedge 01\bar{1}$	=	45 24	45 20
$a \wedge d$, $100 \wedge 011$	=	87 57	88 6
$e \wedge d$, $101 \wedge 011$	=	80 8½	80 10½
$p \wedge p$, $112 \wedge \bar{1}1\bar{2}$	=	83 8	83 0

Axes $= a : b : c = 2.188 : 1 : 2.403$. $\beta = 100 \wedge 001 = 85° 6'$.

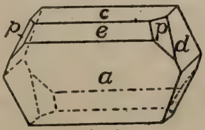


Fig. 6.

The crystals of formanilide were for the most part imperfect and gave poor reflections. Acetanilide has been measured by Bücking,[1] and was found to be orthorhombic, the axes $a : c = 0.848 : 2.067$.

New Haven, May, 1897.

Contributions from the Chemical Laboratories of the Massachusetts Institute of Technology.

XVII.–SYNTHESIS OF HEXAMETHYLENE-GLYCOL DIETHYL ETHER AND OTHER ETHERS FROM TRIMETHYLENE GLYCOL.

By Arthur A. Noyes.

INTRODUCTION.

The following investigation was undertaken originally with the hope of preparing the hydrocarbon hexamethylene[2] from compounds of the fatty series. Although this object has not been attained, yet the syntheses which have been effected seem of sufficient interest to merit publication.

Trimethyleneglycol formed the starting point in this investigation. This substance was discovered last year by Noyes and Watkins[3] to exist as an accidental impurity in a sample of low-gravity glycerin recovered from soap-lye, and a considerable quantity of it was obtained from that source. It was submitted to the series of reactions that are represented by the following equations, hexamethyleneglycol diethyl ether, $C_2H_5O.(CH_2)_6.OC_2H_5$, being finally obtained :

$$CH_2OH.CH_2.CH_2OH + Na = CH_2OH.CH_2.CH_2ONa + H;$$

$$CH_2ONa.CH_2.CH_2OH + C_2H_5I = C_2H_5O.(CH_2)_3.OH + NaI;$$

$$3C_2H_5O.(CH_2)_3.OH + PCl_3[Br_3][I_3] = 3C_2H_5O.(CH_2)_3.Cl[Br][I] + PO_3H_3.$$

$$2C_2H_5O.(CH_2)_3.Cl[Br][I] + 2Na = C_2H_5O(CH_2)_6.OC_2H_5 + 2NaCl[Br][I].$$

Hexamethyleneglycol diethyl ether was also probably obtained, though not in a state of purity, from the ethyl brompropyl ether by the following series of reactions :

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[1] Jahresb. 1877, 679.

[2] Cf. Baeyer : Ann. Chem., **278**, 110.

[3] J. Am. Chem. Soc., **17**, 890.

$C_2H_5O.(CH_2)_3.Br + KCN = C_2H_5O.(CH_2)_3.CN + KBr.$

$C_2H_5O.(CH_2)_3.CN + KOH + H_2O = C_2H_5O.(CH_2)_3.CO_2K + NH_3$

$2C_2H_5O.(CH_2)_3.CO_2K + 2H_2O$ (electrolyzed) $=$

$C_2H_5O.(CH_2)_6.OC_2H_5 + 2KHCO_3 + H_2.$

In addition to the compounds involved in these syntheses, a number of others have been prepared from the ethyl γ-brompropyl ether. As the reactions of halogenated ethers have been but little investigated, the results may be of interest. The malonic-ether and Fittig syntheses have both been successfully carried out with the brom-ether referred to.

The separate preparations will be described in detail in the following pages :

Trimethyleneglycol Monoethyl Ether, $CH_2OH.CH_2.CH_2.OC_2H_5$.

In the first attempts to prepare this substance, the theoretical quantity (one atomic weight of sodium), was dissolved in one molecular weight of glycol with the aid of heat, and the product was then heated on a water-bath with an excess of ethyl iodide. The sodium glycolate formed was completely solid, and the ethyl iodide acted very slowly upon it. The result was entirely unsatisfactory.

It was, however, found that by employing about half the theoretical quantity of sodium a fairly good yield was obtained. To 300 grams of glycol in a 500 cc. distilling-flask 42 grams of very thin-cut sodium are added continuously in small portions so that the temperature of the mixture is maintained at, but not much above, the melting-point of the sodium. If the addition is made too rapidly, violent heating attended by decomposition, results. If too slowly, the action ceases, and external heat must be applied to start it again, an operation often attended with serious frothing. Only towards the very end of the reaction is it sometimes necessary to heat gently over a free flame to dissolve the last of the sodium. The product, when cold, is a yellow transparent, barely fluid mass. The flask containing it, provided with a long return-cooler, is heated in a water-bath, and 318 grams of ethyl iodide are added, cautiously at first. The mixture is heated for two or three hours longer, and is then submitted to distillation in an oil-bath, at first at ordinary and finally under greatly reduced pressure. For the complete distillation several hours are necessary. The distillate is then fractionated at ordinary pressure, a tower being used up to 190°. The principal fractions boiled between 70° and 90°, 150°–170°, and 210°–215°. In some cases a considerable amount of material boiling above 230° was also formed. The first fraction consisted mainly of unchanged ethyl iodide and ethyl alcohol, the second of the monoethyl ether, and the third of the glycol. From 600 grams of glycol 234 grams of the ether boiling between 150° and 170°, and 341 grams of recovered glycol were obtained. The yield referred to the glycol consumed is 66 per cent. of the theoretical. The portion boiling between 150°–170° was repeatedly refractionated, and it finally boiled almost wholly between 159° and 162°. The fraction from 160°–161° (corr.) was analyzed with the following results :

0.3811 gram of substance gave 0.8040 gram CO_2 and 0.3970 gram H_2O.

	Calculated for $C_5H_{12}O_2$.	Found.
C	57.69	57.58
H	11.59	11.66

The trimethylene-glycol monoethyl ether is a colorless, pleasant-smelling liquid, miscible with water in all proportions. Its specific gravity at $\frac{25^\circ}{25^\circ}$ was found to be 0.915, and its index of refraction at 25°, 1.416. Its boiling-point is 160°–161° (corr.) at 760 mm.

Trimethylene-glycol Diethyl Ether

$C_2H_5O.CH_2.CH_2.CH_2.OC_2H_5$.

(With H. M. CHASE.)

The diethyl ether was prepared from the monoethyl ether by a process exactly similar to that described above, 55 grams of monoethyl ether, 6 grams of sodium, and 45 grams of ethyl iodide being used. The distillate boiling above 100° was washed repeatedly with water to remove the monoethyl ether, dried with potassium carbonate, and distilled. The portion from 130°–150° was allowed to stand over sodium, nad was then twice distilled from it.

The product, consisting of 5 grams, finally distilled mainly between 140°–141° (corr.) at 760 mm., and was submitted to analysis with results as follows :

0.4154 gram substance gave 0.9609 gram CO_2 and 0.4554 gram H_2O.

0.3231 gram substance gave 0.7485 and 0.3496 gram H_2O.

	Calculated for $C_7H_{16}O_2$.	Found. I.	II.
C	63.58	63.14	63.23
H	12.20	12.27	12.11

The diethyl ether possesses a fruity odor, and is insoluble in water. The specific gravity at $\frac{25^\circ}{25^\circ}$ is 0.835.

Ethyl γ-Chlorpropyl Ether, $CH_2Cl.CH_2.CH_2.OC_2H_5$.

This compound was prepared by the action of phosphorus trichloride on trimethyleneglycol monoethyl ether. To 82 grams of the latter 49 grams of the former were gradually added, the mixture allowed to stand for some hours in cold water, and then heated on a water-bath for one hour. The product was poured into water, washed, dried with calcium chloride, and distilled. 50 grams of the chlorether boiling between 125° and 135° were obtained, or about 50 per cent. of the theoretical yield.

Subsequent fractionation showed that the true boiling-point is 130°–131 (corr). The specific gravity at $\frac{25^\circ}{25^\circ}$ was found to be 0.957.

The compound was analyzed with the following result :

0.3643 gram substance gave 0.6552 gram CO_2 and 0.3096 gram H_2O.

0.3887 gram substance gave 0.7060 gram CO_2 and 0.3239 gram H_2O.

	Calculated for $C_5H_{11}ClO$.	Found. I.	II.
C	48.98	49.07	49.57
H	9.04	9.53	9.32

Ethyl γ-Brompropyl Ether, $CH_2Br.CH_2.CH_2.OC_2H_5$.

The method of preparation was the same as in the case of the preceding compound. Equal quantities (105 grams of each) of phosphorus tribromide and the monoethyl ether were used. From 210 grams of the latter worked in two separate operations 246 grams of the bromether boiling between 148° and 153° were obtained, amounting to 73 per cent. of the theoretical yield. It is advisable in order to avoid decomposition to fractionate the ether under reduced pressure with the help of a tower. A small quantity of ethyl bromide and of trimethylene bromide is always formed in the reaction.

The ethyl brompropyl ether is an aromatic-smelling liquid insoluble in water. Its boiling-point is 150°–151°, and its specific gravity at $\frac{25^\circ}{25^\circ}$ is 1.300. An analysis of the ether was made by Mr. L. H. Goodhue with the following results:

0.2025 and 0.2495 gram substance gave respectively 0.2300 and 0.2828 gram AgBr.

	Calculated for $C_6H_{11}BrO$.	Found. I.	II.
Br	47.83	48.30	48.20

The results are slightly high, probably owing to the presence of a small amount of trimethylene bromide, which could not be separated by fractionation.

Ethyl γ-Iodopropyl Ether, $CH_2I.CH_2.CH_2.OC_2H_5$.

(With GRACE A. VANEVEREN.)

This ether was first prepared by a method similar to that used for the corresponding chlor- and bromethers, that is to say, by the action of phosphorus di-iodide[1] on trimethylene glycol monoethyl ether. To 60 grams of the latter compound contained in a flask surrounded with ice-water 100 grams of the di-iodide were gradually added, and the mixture was then heated on a water-bath for an hour. The resulting liquid was poured into water, washed, taken up with ether, dried with calcium chloride, and repeatedly fractionated under a pressure of 150 mm.

The product, consisting in two preparations of 30 and 40 grams respectively, distilled mainly between 130° and 134° at the pressure just mentioned, and proved to be the ethyl iodopropyl ether. This substance is a colorless liquid, turning brown on standing, possessing an odor exactly like that of the corresponding chlor- and bromethers. Its specific gravity at $\frac{25^\circ}{25^\circ}$ was found to be 1.585. It is completely soluble in cold concentrated sulphuric acid, and separates unchanged from the solution when diluted with water. Carius determinations gave the following results:

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[1] Made as described in Graham-Otto's Lehrbuch der Chemie, 2, 340.

0.2123 and 0.2215 gram substance gave respectively 0.2398 and 0.2488 gram of silver iodide.

	Calculated for $C_5H_{11}IO$.	Found. I.	II.
I	59.30	61.05	60.70

The somewhat too high results are probably explained by the presence of a small amount of trimethylene iodide. The yields of the iodether (30 and 40 grams from 60 grams of the glycol monoethyl ether) were not very satisfactory, being only 25 and 33 per cent. of the theoretical yield.

In the hope of getting a better yield, an attempt was made to prepare the ethyl iodpropyl ether by another method, namely by saturating the glycol monoethyl ether at 0° with hydriodic acid, and allowing the mixture to stand, in one case for half an hour and in another for several hours, at the ordinary temperature. It was, however, found that the products (after washing with alkali and drying) had specific gravities of 1.92 and 1.98, respectively, showing that a large proportion of di-iodide had been formed, and that even in the cold the ethoxyl, as well as the hydroxyl, group had been replaced by iodine. As further evidence of this, it may be mentioned that a large amount of a low-boiling iodide (ethyl iodide) was obtained on distilling the product from a water-bath.

Hexamethylene-glycol Diethyl Ether, $C_2H_5O(CH_2)_6OC_2H_5$.

The only investigation known to me of the action of sodium or other metals on halogenated ethers is that of Henry,[1] who experimented with β-ioddiethyl ether in this direction. His experiments were undertaken in the hope of effecting the synthesis of tetramethylene-glycol diethyl ether by the union of the radicals left on the removal of the iodine from two molecules. His experiments were, however, entirely unsuccessful in this respect.

Nevertheless, I thought it worth while to attempt the analogous synthesis of hexamethylene-glycol diethyl ether from the halogenated propyl ethyl ethers. All three of these were therefore treated with sodium. The experiments, which were made in a similar manner in the three cases, were carried out as follows :

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[1] Compt. rend., **100**, 1007.

A third or half more than the theoretical quantity of sodium required for the decomposition of the halogenated ether was cut in thin slices, placed in a flask, and covered with absolute ether ; the total quantity of the halogenated ether was then added at once, and the mixture heated on a water-bath for several hours. The liquid was decanted from the precipitated sodium haloid, filtered, and distilled, a tower being used until the boiling-point reached 70°.

Result with the Chlorether.—The product of the reaction with the chlorether separated into three fractions, boiling from 65°–68°, from 125°–135°, and 207°–209° (corr.) at the ordinary pressure.

The last portion, as will be seen later, consisted of hexamethylene-glycol diethyl ether. It was, however, very small in amount, only 3½ grams having been obtained from 72 grams of chlorether worked in two operations. Its specific gravity at $\frac{25^\circ}{25^\circ}$ was found to be 0.847.

The fraction boiling from 125°–135° was unchanged chlorether. That from 65°–68° was, however, evidently a product of the reaction. Its odor was exactly like that of ordinary ethyl ether ; it was not miscible with water, and did not decolorize bromine water ; its specific gravity was 0.727. These facts showed that the body was probably ethyl propyl ether, whose boiling-point is 64°, and whose specific gravity is 0.735 at 20°.

The reaction was carried out several times under various conditions (of temperature and proportions of the sodium, chlorether, and ordinary ether), but no better yield of hexamethylene-glycol diethyl ether than that above mentioned could be obtained.

Result with the Bromether.—In the case of the ethyl brompropyl ether the result was somewhat more satisfactory. The reaction-product resolved itself mainly into two fractions, boiling from 130°–150° and from 200°–220°.[1] In one experiment in which 83 grams of bromether were employed, the former fraction consisted of 11 cc. and the latter of 9 cc. In a second experiment with 111 grams of bromether they consisted respectively of 18 and 6 cc. In a third operation with a larger amount (214 grams) of bromether, 32 grams of the higher boiling portion, consisting of methyleneglycol diethyl ether, were obtained. This is 28 per cent. of the theoretical yield.

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[1] A small quantity of liquid boiling from 40°–60° lighter than water, insoluble in it, and combining energetically with bromine, was also obtained.

That this high-boiling portion was, in reality, the expected hexamethyleneglycol diethylether is shown by the following analyses made with a portion of the substance purified by fractionation under reduced pressure, since slight decomposition takes place at ordinary pressure.

0.4479 gram substance gave 1.1270 grams CO_2, and 0.5013 gram H_2O.

0.5074 gram substance gave 1.2744 grams CO_2, and 0.5723 gram H_2O.

	Calculated for $C_{10}H_{22}O_2$.	Found. I.	II.
C	68.92	68.66	68.52
H	12.74	12.53	12.62

An attempt to make a vapor density determination by the Victor Meyer method in naphthalene vapor was unsuccessful, owing to rapid decomposition of the substance.

The hexamethylene-glycol diethyl ether, as obtained, was a colorless liquid insoluble in water. It boils at 208° (corr.) at 760 mm., and at 160°–162° (corr.) at 200 mm. Its specific gravity at $\frac{25^\circ}{25^\circ}$ is 0.846. It dissolves in cold concentrated sulphuric acid and is precipitated from the solution by the addition of water. It is slowly acted upon in the cold by sodium with formation of a slimy green solid, and the small yield obtained is no doubt due, at least in part, to this fact. Phosphorus trichloride heated with it on a water-bath for two hours had little or no action upon it.

The original fraction, boiling from 130°–150°, was diluted with ether and boiled with a large excess of sodium to remove all traces of unchanged bromether present in it. On refractionation the product boiled almost wholly between 140° and 143°, and this portion was further examined. Its specific gravity was 0.797. It contained 70.8 per cent. of carbon, 12.4 per cent. of hydrogen, and 16.8 per cent. of oxygen. Its vapor density determined in naphthalene vapor was 2.85, corresponding to a molecular weight of 82. Its behavior with cold concentrated sulphuric acid showed it, however, to be a mixture. It dissolved completely in that reagent, but on dilution with water only one-fourth of the original liquid precipitated, the remainder having combined chemically with the acid. The precipitated portion was evidently an ether, probably trimethylene-glycol diethyl ether, which corresponds in odor and boiling-point with those shown by this substance. Its formation from the ethyl brompropyl ether is readily explained by the assumption that sodium ethylate was produced in the sodium reaction either from alcohol present in the absolute ether employed or by decomposition of the bromether itself.

The nature of the other and main constituent of the 140°–143° fraction could not be determined. It was evidently an unsaturated body, for the original liquid decolorized instantly aqueous bromine, and also a solution of iodine. It is remarkable that with dry bromine hydrobromic acid was copiously evolved, showing that substitution also took place.

Result with the Iod-ether.—The product was boiled with a small amount of alcoholic potash to free it entirely from unchanged iod-ether; it was then precipitated from the solution by the addition of water, and was dried and distilled. It boiled between 157° and 162° at 200 mm. pressure and had a specific gravity of 0.843 at $\frac{22^\circ}{20^\circ}$. It gave the following results on analysis:

0.2668 gram substance gave 0.6643 gram CO_2, and 0.2844 gram H_2O.

0.3004 gram substance gave 0.7493 gram CO_2 and 0.3424 gram H_2O.

	Calculated for $C_{10}H_{22}O_2$.	Found. I.	II.
C	68.90	67.94	68.08
H	12.73	11.92	12.75

Three grams of the hexamethyleneglycol diethyl ether were obtained from 25 grams of the iodoether, which is 30 per cent. of the theoretical yield.

γ-Ethoxybutyric Acid, $C_2H_5O(CH_2)_3CO_2H$.

(With L. H. GOODHUE.)

In order to effect the synthesis of hexamethylene-glycol diethyl ether by the second process outlined in the introduction, it was first necessary to prepare the *γ*-ethoxybutyric acid. This body had been previously made by Fittig and Ström[1] by the action of sodium ethylate on butyrolactone. We succeeded in obtaining it in moderate yield by the action of potassium cyanide on *γ*-brompropyl ethyl ether and subsequent saponification of the nitrile.

Fifty grams of the bromether were dissolved in a small quantity of alcohol, a concentrated aqueous solution of 22 grams of pure potassium cyanide (15 per cent. more than the theoretical quantity) was added, and the mixture, which consisted of two separate layers, heated in a boiling water-bath for four hours. The nitrile was not isolated, but was directly saponified by decanting the liquid containing it from the potassium bromide which had separated, adding an excess of solid caustic potash and a little water, and heating on a water-bath as long as ammonia was evolved. The alcohol was then distilled off and the solution acidified with strong hydrochloric acid, decanted from the precipitated potassium chloride, and extracted 15 times with ether.

The ether solution was dried with calcium chloride and distilled. After the removal of the ether the thermometer rose rapidly to 230°, and the product distilled almost entirely between 230° and 240° (corr.).

The properties of the product are identical with those described by Fittig and Ström, who give 232° as its boiling-point. It is a colorless liquid soluble in water.

In two separate preparations 10 grams and 15 grams of the acid were obtained from 50 and 75 grams, respectively, of the bromether, constituting in each case 25 per cent. of the theoretical yield. In another preparation, on a smaller scale (in which 15 grams of the bromether were employed) a 42 per cent. yield was obtained. The poor yield is mainly owing to the fact that a considerable portion of the ether is carbonized or resinified by the action of the potassium cyanide.

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[1] Ann. Chem. (Liebig), **267**, 200.

Electrolysis of γ-Ethoxybutyric Acid.

(With L. H. Goodhue.)

The electrolysis of the acid was carried out according to the method described by Crum Brown, and Walker,[1] and used by them in the synthesis of the compound ethers of dibasic acids.

Fifteen grams of the γ-ethoxybutyric acid were neutralized with potassium carbonate and the resulting salt dissolved in the smallest possible quantity of water. The solution was placed in a large platinum crucible, which served as the cathode, and a thick platinum wire, in the form of a spiral, was placed in the center to act as an anode. The crucible was surrounded with ice-water, and a current of 3 amperes was passed through for an hour and a half. The oily layer which had formed was separated in a separatory funnel from the aqueous solution, which latter was used for dissolving another portion of the ethoxybutyric acid to be electrolyzed. The oily layer was dried with calcium chloride and submitted to distillation under a reduced pressure of 195 mm. It did not boil very constantly at first, but a portion of 4 grams was obtained after several fractionations, distilling between 155° and 165°. The quantity was not sufficient to admit of complete purification, and the following analyses will be seen to correspond only very roughly with the values calculated for hexamethyleneglycol diethyl ether.

0.3404 gram substance gave 0.8074 gram CO_2, and 0.3594 gram H_2O.

0.3085 gram substance gave 0.7355 gram CO_2, and 0.3299 gram H_2O.

	Calculated for $C_{10}H_{22}O_2$.	Found. I.	Found. II.
C	68.90	64.74	65.06
H	12.73	11.82	11.97

But considering also the agreement of the boiling-point with that shown by the ether prepared by the sodium reaction above described, there is little doubt that the product consisted in the main of hexamethylene-glycol diethyl ether.

The yield was, however, small, only 4 grams of the ether being obtained from 30 grams of acid, which is 20 per cent. of the theoretical.

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[1] Ann. Chem. (Liebig), **261**, 107.

Attempt to Prepare a Metallic Derivative from the Ethyl Brompropyl Ether.

(With L. H. GOODHUE.)

No attempt has been made to our knowledge to prepare a metallic derivative of a hydrocarbon radical containing the ether grouping. We therefore investigated the action both of sodium amalgam and of the zinc-copper couple on ethyl brompropyl ether, carrying out the reactions in the manner usually followed in the preparation of mercury and zinc ethyl. The metals had no action on the bromether in the cold; they were therefore heated with it in a water-bath for several hours, a little ethyl acetate being added to promote the reaction. Even under these circumstances the action was slight, and no evidence of the formation of a metallic compound could be obtained either by distillation under reduced pressure, by extraction with ether, or by treatment with water. The presence of the ether grouping seems therefore to prevent the union of the hydrocarbon radical with metals.

Ethyl γ-Phenylpropyl Ether, $C_6H_5.CH_2.CH_2.CH_2.OC_2H_5$.

(With H. H. TOZIER.)

The following experiments were made in order to determine whether the Fittig reaction can be carried out satisfactorily with a halogenated ether.

45 grams of sodium and 150 cc. of absolute ether were placed in a flask surrounded with ice-water, and a mixture of 95 grams of ethyl brompropyl ether and 114 grams of brombenzene was added in small portions, since the action when once started becomes very violent. After standing twenty-four hours the ether was distilled off on a water-bath, and the residue was then heated in an oil-bath, the pressure within the flask being reduced to 40–50 mm. The distillate was repeatedly fractionated at ordinary pressure. The principal fraction obtained boiled constantly between 222° and 226° (corr.), and consisted of 47.5 grams. The adjacent fractions (218°–222° and 226°–230°) together contained only 2.5 grams. The yield (50 grams) is 54 per cent. of the theoretical amount obtainable from the bromether taken. That this substance consisted of the expected ethyl phenylpropyl ether is shown by the following analysis:

0.2135 gram substance gave 0.6279 gram of CO_2 and 0.1879 gram of H_2O.

0.2312 gram substance gave 0.6821 gram of CO_2 and 0.2023 gram of H_2O.

	Calculated for $C_{11}H_{16}O$.	Found.	
		I.	II.
C	80.45	80.26	80.52
H	9.82	9.85	9.79

Ethyl γ-phenylpropyl ether is a liquid of terpene-like odor of boiling-point 224° (corr.) and specific gravity 0.924 at $\frac{15^\circ}{15^\circ}$.

In addition to this product, 27 grams of a liquid boiling quite uniformly between 80° and 150° were obtained, but even after a second treatment with sodium no constant-boiling substance could be separated from it.

γ-Ethoxypropyl-malonic Ether,

$C_2H_5O.(CH_2)_3.CH.(CO_2C_2H_5)_2$.

(With C. H. Stone.)

The introduction of the radical of the ethyl brompropyl ether into malonic ether was effected in the usual manner. 48 grams of malonic ether were added to the solution of 6.9 grams of sodium in alcohol, and 50 grams of ethyl brompropyl ether gradually poured in. The mixture was then heated on a water-bath for three hours, after which the alcohol was distilled off and the residue submitted to distillation in a metal-bath under reduced pressure. The distillate was fractionated at ordinary pressure. A portion of 25 grams boiling between 270° and 275° (corr.) was thus obtained. Analysis showed it to be pure ethoxypropyl-malonic ether.

0.2104 gram substance gave 0.4505 gram CO_2 and 0.1707 gram H_2O.

0.2321 gram substance gave 0.4975 gram CO_2 and 0.1852 gram H_2O.

	Calculated for $C_{12}H_{22}O_5$.	Found.	
		I.	II.
C	58.52	58.44	9.10
H	9.00	58.50	8.93

The ether thus prepared is a nearly odorless liquid, insoluble in water, of specific gravity 1.016 at $\frac{15^\circ}{15^\circ}$, and of boiling-point 273° (corr.).

The yield (25 grams from 50 grams of the bromether) is 34 per cent. of the theoretical quantity.

δ-Ethoxyvalerianic Acid, $C_2H_5O.(CH_2)_4.CO_2H$.

(With C. H. STONE.)

The ether just described was converted into δ-ethoxyvalerianic acid by boiling it with strong potassium hydrate solution (1 : 2) till the oil dissolved, acidifying the solution with hydrochloric acid, extracting a large number of times with ether, distilling off the ether, and heating the remaining liquid in an oil-bath to 170° (for about four hours) as long as carbon dioxide escaped. The impure product was fractionated and was found to resolve itself almost wholly into two fractions nearly equal in amount, and boiling from 247° to 257° (corr.), and from 209° to 212° (corr.) respectively. The former portion consisted of δ-ethoxyvalerianic acid, as its properties and the following analyses showed :

0.1738 gram substance gave 0.3647 gram CO_2 and 0.1502 gram H_2O.

0.2229 gram substance gave 0.4705 gram CO_2 and 0.1958 gram H_2O.

	Calculated for $C_7H_{14}O_3$.	Found. I.	II.
C	57.50	57.25	57.58
H	9.58	9.68	9.83

The acid is a colorless liquid, soluble in water, of specific gravity 0.994, and boiling-point 252°. A 37 per cent. yield was obtained in its preparation as above described.

The nature of the compound composing the lower-boiling fraction could not be fully determined with the amount at our disposal. It was insoluble in water and in sodium carbonate solution. It was therefore completely freed from ethoxyvalerianic acid by washing with a solution of sodium carbonate. The following analyses show that it agrees approximately in percentage composition with the formula $C_7H_{14}O_3$, which would make it an isomer of ethoxyvalerianic acid.

0.1848 gram substance gave 0.3960 gram CO_2 and 0.1563 gram H_2O.

0.3181 gram substance gave 0.6791 gram CO_2 and 0.2708 gram H_2O.

	Calculated for $C_7H_{14}O_3$.	Found. I.	II.
C	57.50	58.48	58.28
H	9.58	9.46	9.53

The liquid was unacted upon by sodium in the cold, and very slightly, if at all, by a solution of potassium hydrate at 100°. It dissolved instantly in cold concentrated sulphuric acid, and was precipitated from the solution on the addition of water. These reactions indicate that the substance is a simple ether, but no probable formula corresponding to the above analytical results, can be assigned to it.

Summary.

The results of this investigation may be briefly summarized as follows:

The monoethyl ether of trimethylene-glycol is readily prepared by the action of sodium and ethyl iodide on the glycol; but it is essential that the glycol be used in considerable excess. The diethyl ether of the glycol has been prepared from the monoethyl ether, but not from the glycol itself, by an exactly similar process.

By the action of phosphorus trichloride, tribromide, and diiodide on the monoethyl ether, the hydroxyl group was replaced by halogen with the production of the ethyl chlor-, brom-, and iod-propyl ethers. The yields obtained were about 50, 75 and 30 per cent. respectively in the three cases. Hydriodic acid gas at 0° caused replacement of the ethoxyl as well as the hydroxyl group.

The diethyl ether of hexamethylene-glycol was found to be produced in very small quantity by the action of sodium on an ethereal solution of ethyl chlorpropyl ether and in somewhat larger quantity by the similar reaction with the corresponding brom and iodo ethers; but the best yields obtained did not exceed 30 per cent. of the theoretical.

By heating the ethyl brompropyl ether in a water-bath for several hours, first with a slight excess of concentrated aqueous potassium cyanide solution, and then with concentrated potash and acidifying, γ-ethoxyvalerianic acid was obtained in a 40 per cent. yield. It was shown that by the electrolysis of the salt of this acid a small quantity of hexamethylene-glycol diethyl ether is probably formed.

Attempts to prepare a metallic derivative by the action of sodium amalgam and of the zinc-copper couple on the ethyl brompropyl ether were entirely unsuccessful.

The Fittig synthesis was successfully carried out with this bromether and brombenzene, a 54 per cent. yield of ethyl γ-phenylpropyl ether being obtained.

The ethoxypropyl radical was also readily introduced into malonic ether by heating its sodium compound with the ethyl brompropyl ether, the yield being 34 per cent. The substituted malonic ether so obtained gave, on saponification and subsequent heating to 170° of the acid separated from its salt, δ-ethoxyvalerianic acid in a 37 per cent. yield. Another substance was produced in this reaction in considerable quantity, but its nature was not determined.

The following table presents a summary of the boiling-points and specific gravities of all the compounds described for the first time in this article. The boiling-points are those corresponding to the ordinary atmospheric pressure of about 760 mm., except when otherwise indicated. The specific gravities refer to 25° unless otherwise indicated, the water being measured at the same temperature.

Substance.	Boiling-point.	Specific gravity.
$C_2H_5O.CH_2.CH_2.CH_2OH$.	160°–161°.	0.915
$C_2H_5O.CH_2.CH_2.CH_2.OC_2H_5$.	140°–141°.	0.835
$C_2H_5O.CH_2.CH_2.CH_2Cl$.	130°–131°.	0.957
$C_2H_5O.CH_2.CH_2.CH_2Br$.	150°–151°.	1.300
$C_2H_5O.CH_2.CH_2.CH_2I$.	130°–134° (at 150 mm.)	1.585
$C_2H_5O.(CH_2)_6.OC_2H_5$.	208°; 160°–162° (at 200 mm.)	0.845
$C_2H_5O.(CH_2)_4.COOH$.	252°	0.994
$C_2H_5O.(CH_2)_3.CH(CO_2C_2H_5)_2$.	273°	1.016[1]
$C_6H_5.(CH_2)_3.OC_2H_5$.	224°	0.924[1]

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS., MAY, 1897.

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[1] At 15°.

ON THE CHLORONITRIDES OF PHOSPHORUS. (II).[1]

BY H. N. STOKES.

In a former article[2] I have shown that in addition to the phosphonitrilic chloride,[3] $P_3N_3Cl_6$, discovered by Liebig, there exists another, $P_4N_4Cl_8$, of similar properties, which is formed at the same time, but in smaller quantity. The opinion was expressed that these bodies belong to a series of polymers, $(PNCl_2)_n$, the existence of other members of which was indicated by the formation, in small amount, of a liquid of the same empirical composition.[4] The yield of this secondary product, only 2 per cent. of the theoretical or 1 per cent. of the pentachloride used, was too small to allow of its preparation in quantities large enough to admit of the isolation of its supposed constituents, but a fractional distillation of the few grams at my disposal showed that it contained crystalline substances of higher boiling-points than those of the two bodies thus far known.

The method of preparation then employed consisted in distilling phosphorus pentachloride with a large excess of ammonium chloride in a retort, at atmospheric pressure; it offered but little prospect of obtaining the higher members. The total yield of phosphonitrilic chloride was but 15 per cent. of the theoretical, most of the pentachloride being converted into "phospham" by the excess of ammonium chloride, while only those members could be obtained which distil unchanged at atmospheric pressure. Decreasing the amount of ammonium chloride resulted only in a loss of pentachloride by volatilization, without increasing the yield of the bodies sought after.

The following method has been found to give entirely satisfactory results; several new bodies have been obtained, and the simpler phosphonitrilic chlorides, at least, are now easily accessible substances: If equal molecular weights of phosphorus pentachloride and ammonium chloride be heated in a sealed tube, there results a mixture of chloronitrides, which is partly crystalline and soluble in gasoline, but for the greater part liquid and insoluble in this solvent, and of a high degree of complexity. This may be distilled almost without residue, the distillate being a crystalline mass, impregnated with an oil, and composed almost wholly of a mixture of members of the series $(PNCl_2)_n$ in nearly theoretical amount, containing about 50 per cent. $P_3N_3Cl_6$, and 25 per cent. $P_4N_4Cl_8$, the remainder consisting of the higher homologues. From this distillate the new bodies, with one exception, have been isolated.

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[1] Published by permission of the Director of the United States Geological Survey.

[2] This JOURNAL, **17**, 275 (1895): Ber. d. chem. Ges., **28**, 437.

[3] I propose in future to use the term *phosphorus chloronitride* to denote any body composed of phosphorus, nitrogen, and chlorine, the name *phosphonitrilic chloride* being reserved for chloronitrides belonging to the series $(PNCl_2)_n$.

[4] This JOURNAL, **17**, 277, 280, 290.

The series, as at present known, consists of the following :[1]

		Melting-point.	Boiling-point.	
			13 mm.	760 mm.
Triphosphonitrilic chloride,	$(PNCl_2)_3$	114°	127°	256.5°[2]
Tetraphosphonitrilic chloride,	$(PNCl_2)_4$	123.5°	188°	328.5°[3]
Pentaphosphonitrilic chloride,	$(PNCl_2)_5$	40.5–41°	223–224.3°	Polymerizes
Hexaphosphonitrilic chloride,	$(PNCl_2)_6$	91°	261–263°	Polymerizes
Heptaphosphonitrilic chloride,	$(PNCl_2)_7$	Liquid at –18°	289–294°	Polymerizes
……				
Polyphosphonitrilic chloride,	$(PNCl_2)x$	Below red heat.	Depolymerizes on distillation.	

There were obtained, further, a liquid residue of the same empirical composition, of a *mean* molecular weight corresponding nearly to $(PNCl_2)_{11}$, and a small amount of a chloronitride, $P_6N_7Cl_9$, not belonging to the above series. The absence of the lower members, $PNCl_2$ and $(PNCl_2)_2$, is remarkable, and theoretically significant. Indications of a trace of a substance more volatile than the compound $(PNCl_2)_3$ and of similar but stronger odor, were observed, but there is no evidence that it consists of one of the missing bodies.

One of the most remarkable properties of the phosphonitrilic chlorides is that each member of the series is converted by heat into the rubber-like *polyphosphonitrilic chloride*, a body, or mixture of bodies, of very high molecular weight, which is highly elastic and insoluble in all neutral solvents, but which swells enormously in benzene, and which, on distilling at a higher temperature, breaks down into a mixture of all the lower members mentioned above, which can then be separated by appropriate means. In this way it is possible to convert any phosphonitrilic chloride quantitatively into any other by

[1] The melting- and boiling-points are corrected.

[2] 183.8° at 100 mm.

[3] 242° at 100 mm.

heat and distillation alone. In preparing any desired member, therefore, we are not limited to the quantity obtained from the first reaction product, but may work the residues over and over again until completely converted into the body sought after. With the exception of a few cases, in which the number of members is limited, as the aldehydes and cyanic acids, this series is therefore unique; I know of no other series of inorganic compounds in which this is possible. Polymerization takes place slowly, but perceptibly, at 250°, and is almost instantaneous at 350°, while depolymerization begins at about 350°, and is rapid at a temperature close to incipient red heat. Triphosphonitrilic chloride, $P_3N_3Cl_6$, is the only member which can be distilled in considerable amount at atmospheric pressure without considerable polymerization and even this polymerizes almost completely on long boiling; at 760 mm. pressure the tetra-compound, $P_4N_4Cl_8$, boils at 328°.5, a temperature at which polymerization occurs quite rapidly, but this, as well as the penta-compound, $P_5N_5Cl_{10}$, and the hexa-compound, $P_6N_6Cl_{12}$, can readily be distilled at 13 mm.; the hepta-compound, $P_7N_7Cl_{14}$, suffers marked polymerization on distilling even at this pressure, and its isolation is therefore attended with much loss. Owing to the rapid change at higher temperatures, I have been unable to isolate any of the higher members, which remain as a considerable oily residuum, and there seems to be but little probability of this being effected by any known method, unless by distilling in a nearly absolute vacuum.

The greatest difficulty in the separation of the members is caused by polymerization. It requires but a small amount of polyphosphonitrilic chloride to cause the liquid to thicken or gelatinize, and therefore to be incapable of further distillation, and some of this body is always formed in the course of a prolonged fractioning of the higher members. It was found, however, that this polymer is much more easily attacked by water than the lower members; when signs of polymerization are observed, it is only necessary to interrupt the distillation, and heat the residue for some time with water, when the resulting oil is again in a condition to continue fractioning. The loss in this operation is small, but the tediousness of a fractional distillation is thereby extraordinarily increased.

It is noteworthy that no regular progression exists in the melting-points of the phosphonitrilic chlorides, and the same is true of their solubility in the ordinary neutral solvents, but the solubility varies in the same sense as the fusibility. Of the members of known molecular weight, the second, tetraphosphonitrilic chloride, is the least soluble and has the highest melting-point, while the corresponding tetrametaphosphimic acid is the least soluble and most stable of the derived acids. With respect to their stability towards water, the new members (polyphosphonitrilic chloride excepted) resemble those already described, being scarcely attacked by prolonged boiling. In ethereal solution, however, there is a perceptible decrease of stability towards water as we rise in the series, a fact already noted with regard to the first two members.[1]

Notwithstanding the high molecular weight of the bodies isolated, no indication of isomers has been observed, although the fractioning was carried out very thoroughly up to 300° at 13 mm.

The investigation will be continued with the object of obtaining the metaphosphimic acids, and, if possible, the two missing lowest members of the phosphonitrilic chloride series; the right of further investigation in this field, however, is *not* reserved.

Experimental Part.

A mixture (which need not be very intimate) of 4 parts perfectly dry phosphorus pentachloride and 1 part ammonium chloride, as required by the equation

$$PCl_5 + NH_4Cl = PNCl_2 + 4HCl,$$

is introduced into an ordinary "bomb" tube, which has previously been drawn out to a neck. It is practicable to fill the tube entirely to the neck, so that the charge for a tube of ordinary dimensions is about 125 grams, yielding 50–55 grams of chloronitrides. After sealing, the length of the neck, exclusive of the rather long capillary, should be about 10 cm. As the mixture liberates 55 per cent. hydrochloric acid, it is necessary to regulate the heating with great care and to open the tube repeatedly. The temperature of the furnace is allowed to rise to 150°, at which the reaction begins, when the gas is at once shut off, and the tube opened at about 100° (in the furnace!). This operation is repeated several times, the temperature being allowed to rise 1°–2° higher each time. When the evolution of hydrochloric acid has slackened and the contents of the tube are mainly liquid while hot, the temperature may be carried to 200° or higher, until little or no gas is given off. The operation requires care and judgment, but with careful working it is possible to avoid explosions, and to obtain with a four-tube furnace about 200 grams of mixed chloronitrides in sixteen hours.

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[1] This JOURNAL, **17**, 289.

The contents of the tube, after cooling, generally consist of a buttery mass or of a thick yellow liquid filled with fine prisms and plates; if heated much above 200°, the liquid frequently separates into two layers. The crystals are soluble in gasoline, but the bulk of the product remains as an immiscible oil.

The neck of the tube is now bent down, the tube placed in an inclined combustion furnace, and by cautious heating, finally to incipient redness, the contents are distilled out. There remains in the tube a very voluminous, spongy, black residue of inconsiderable weight, due to unavoidable impurities and to the impossibility of causing complete reaction in the sense of the above equation. The distillate consists of a crystalline mass impregnated with a yellow oil, and contains about 95 per cent. of the theoretical amount of phosphonitrilic chlorides, with some phosphorus pentachloride, the chloronitride $P_6N_7Cl_9$, and other substances of unknown nature. Before proceeding further, it is necessary to remove the pentachloride, and for this purpose the distillate is melted, poured into *cold* water, and the flask heated in the water-bath for about two hours, the liquids being mixed by blowing air through them. The chloronitrides are then allowed to clear under the hot water, and forced out by means of a wash-bottle arrangement; a separatory funnel cannot be used, as the substance solidifies in the neck, and if allowed to solidify under the wash water, it absorbs so much of this as to cause annoyance in the subsequent distillation. Special drying before distilling is unnecessary.

The product is then distilled up to 200° at 13–15 mm., using an Anschütz flask, as the distillate solidifies instantly on cooling. The residue, containing the members $P_5N_5Cl_{10}$ up, is set aside for later systematic fractional distillation.[1] The distillate, about 70 per cent., consists essentially of $P_3N_3Cl_6$ and $P_4N_4Cl_8$, which, if desired, may be easily separated by fractional distillation *in vacuo*, followed by crystallization from benzene. This is more convenient than the method of separating by steam.[2] If it is desired to convert it into the higher members, it is placed in a combustion tube bent down at about 20 cm. from the open end, and which it should not fill more than one-half after melting. This is laid in an inclined combustion furnace and heated to gentle boiling of the contents. It is well to heat the tube somewhat strongly at a short distance above the liquid, as superheating the vapor promotes polymerization. The time required for polymerization varies greatly ; pure triphosphonitrilic chloride may require two hours or more ; with the above mixture the time is less, and is shorter the higher the boiling-point ; it is shortened by adding already gelatinized substance, which causes the liquid to thicken, and may then be but a few minutes ; it is also shortened by heating under pressure. Sooner or later the liquid begins to thicken, and finally it is converted into a stiff, transparent mass, with little or no liquid, and generally discolored by traces of organic matter. The tube is then connected with a long-necked receiver, exhausted, and the depolymerization and distillation effected by heating, from the front backward, to incipient redness. This part of the operation proceeds rapidly, as it is only necessary to guard against frothing over, and to ensure complete condensation, the latter being easily effected by having the limb of the tube at least 20 cm. long. 100 grams can be worked up at one time and the tube can be used repeatedly. The residue does not weigh more than a few milligrams. The distillation may also be made at atmospheric pressure, but the yield of higher products is thereby diminished. The distillate, which entirely resembles that first obtained, excepting in containing no phosphorus pentachloride and no $P_6N_7Cl_9$, is distilled as before, the washing being omitted. In this way the whole quantity of material can finally be converted into a mixture of members higher than $P_4N_4Cl_8$.

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[1] This residue contains the small amount of $P_6N_7Cl_9$ formed as a secondary product of the original reagents, and as this is apt to cause inconvenience at a later stage by accumulating with the $P_6N_6Cl_{12}$, it is perhaps well to remove as much as possible at this point. For this purpose the residue is allowed to stand for a day or two at the room temperature, and the crystals removed by sucking out under a good vacuum, best in a large Gooch crucible. The filtrate is cooled for a day or two in a refrigerator, and the new crop of crystals separated in the same way, the filtering flask being allowed to stand in the ice-box. The oily filtrate is set aside, and the united crystalline products distilled up to 240° at 13 mm., whereby most of the $P_5N_5Cl_{10}$ passes over. The residue, consisting of $P_6N_6Cl_{12}$, the small amount of $P_6N_7Cl_9$, and the adhering oil is allowed to crystallize in the refrigerator, and the viscous mass is extracted several times with small amounts of gasoline (boiling at 50°-80°). The residue is boiled with benzene, which extracts the $P_6N_7Cl_9$, which crystallizes on concentrating and cooling. The portion dissolved by the gasoline is worked up with the other residues.

This is the method actually employed, but I am not entirely convinced of its necessity, as it is not possible to remove *all* the $P_6N_7Cl_9$ in this way.

[2] This JOURNAL, **17**, 280.

The united residues boiling above 200° are now submitted to systematic fractional distillation at 13–15 mm., using an Anschütz flask, provided with a "trap," to prevent flowing back. During the first distillation polymerization generally begins when the temperature of the bath has reached 270°, but with later distillations, at a higher temperature, and the higher, the purer the fractions are. When polymerization begins, which is indicated by frothing and thickening, the operation is interrupted and the residue heated in the flask with water in the water-bath until it has completely liquefied, which is assisted by agitation, the oil separated[1] and the distillation continued. It has not been found practicable to continue the distillation at a higher temperature than that obtained by heating the bath to 370°, for the liquid begins to polymerize in a few moments, and but an inconsiderable distillate can be obtained. Moreover, at this temperature the polymer shows signs of breaking down into simpler bodies, and the distillate does not consist only of high-boiling members. The total amount of final residue is not very great, and as shown below consists likewise of phosphonitrilic chlorides of still higher molecular weight. In later distillations from 200° upward, polymerization usually stops the process at 260°–270°, but after appropriate washing, the residue may be

[1] In this case a separatory funnel may be used, as the higher chloronitrides are liquid below 80°.

distilled to a much higher temperature. After 8–10 distillations three main fractions are obtained, which are then worked up separately. As $P_5N_5Cl_{10}$, though crystalline, is extremely soluble, it is necessary to carry out the distillations with the first main fraction until a practically sharp boiling-point is obtained, in which connection it may be noted that at 17–20 mm. a change of 1 mm. pressure causes a change of about 1° in the boiling-point, and at 13 mm. a change of about 2°. $P_7N_7Cl_{14}$, being liquid, must also be isolated by distillation only, but at its boiling-point polymerization is so rapid that great loss ensues during a series of distillations. The final purification of $P_6N_6Cl_{12}$ can be effected by repeated recrystallization from benzene, combined with treatment with gasoline to remove the $P_6N_7Cl_9$, which always accompanies it, having nearly the same boiling-point; a complete separation of these two bodies can scarcely be effected by distillation alone.

Owing to many modifications introduced in developing the above method, no accurate statement of the yield can be given; the final product was about 225 grams $P_5N_5Cl_{10}$, 110 grams $P_6N_6Cl_{12}$, 10 grams $P_7N_7Cl_{14}$, and 5 grams $P_6N_7Cl_9$.

Analytical Methods.—With the exception of polyphosphonitrilic chloride, the chloronitrides were analyzed by decomposing in the following manner:

For *phosphorus*, by warming with alcohol and a little ammonia in a platinum crucible until completely dissolved, evaporating to dryness and heating to fuming for an hour with strong sulphuric acid, the crucible being kept covered.

For *nitrogen*, by treating as above, omitting the ammonia.

For *chlorine*, by heating with alcohol and ammonia. It is necessary to precipitate with silver nitrate in the presence of a large volume of 10 per cent. nitric acid and to filter hot, in order to avoid the formation of silver metaphosphimates, which are difficultly soluble in dilute nitric acid.

In decomposing polyphosphonitrilic chloride, which is attacked by water alone, the alcohol was omitted. The method of Carius was used for determining chlorine, as it was found that otherwise compounds insoluble in dilute nitric acid were formed. For the other chloronitrides this method offers no advantage.

Molecular weight determinations were made by the boiling-point method with the apparatus of Hite,[1] using as solvent carefully purified and dried benzene.[2]

Pentaphosphonitrilic Chloride, $P_5N_5Cl_{10}$.—This body, carefully purified by fractional distillation, as described above, gave on analysis :

	Calculated for $P_5N_5Cl_{10}$.	Found.
P	26.75	26.87
N	12.11	12.05
Cl	61.14	61.42

Ratio, P : N : Cl = 1 : 0.99 : 2.00.

Molecular Weight. Solvent : Benzene.

Grams solvent.	Grams substance.	Elevation.	Molecular weight found.	Percentage variation from theoretical.
46.49	1.4688	0.137°	619	+6.2
"	2.9439	0.287°	589	+1.6
"	4.4337	0.437°	583	+0.5

Calculated for $P_5N_5Cl_{10}$, 579.8.

Pentaphosphonitrilic chloride fuses at 40°.5–41°, and boils at 223°–224°.3 (corr.) at 13 mm. Its vapor is without the pronounced and characteristic aromatic odor possessed by that of triphosphonitrilic chloride. At its melting-point, it is miscible in all proportions with benzene, gasoline, ether and carbon disulphide, and cannot be recrystallized from any of these solvents; in fact, small fragments liquefy instantly in their concentrated vapors. Glacial acetic acid also dissolves it quite readily, and from this solution water throws it out as an oil, solidifying at once on touching. It shows a decided tendency to superfusion, especially when not absolutely pure; when left by evaporating its ether or benzene solution, it may remain liquid for days, but solidifies at once on touching with a glass rod, usually to a decidedly crystalline mass, at other times to a transparent glass. The pure substance, when fused, slowly solidifies, long, flat crystals shooting out through the liquid, which are limited only by the size of the vessel, crystals of 10 cm. in length being readily obtained. It contracts greatly on solidifying. When pure, the solidified mass is naturally dry, but the least contamination with other members of the series causes a portion to remain liquid, which is easily detected by crushing on a piece of filter-paper; this is a very good test of its purity. This tendency to superfusion must be borne in mind in separating it by fractional distillation; a nearly pure sample will remain liquid much longer than the higher or lower fractions. In ether solution it is perceptibly more easily attacked by water than the preceding chloronitride, but hot water alone is almost without action.

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[1] This JOURNAL, **17**, 512.

[2] The molecular weight of $P_3N_3Cl_6$ has been determined by the vapor density method (J. Chem. Soc., [2], **2**, 225; This JOURNAL, **17**, 283.) A series of determinations by the boiling-point method gave 346, 350, 353. Calculated 347.9.

Hexaphosphonitrilic Chloride, $P_6N_6Cl_{12}$. — After repeated crystallization from benzene,[1] this gave:

	Calculated for $P_6N_6Cl_{12}$.	Found.
P	26.75	26.98
N	12.11	12.37
Cl	61.14	60.98

Ratio, P : N : Cl = 1 : 1.01 : 1.98.

Molecular Weight. Solvent: Benzene.

Grams solvent.	Grams. substance.	Elevation.	Molecular weight.	Percentage variation from theoretical.
47.12	1.8058	0.152°	673	—3.2
"	3.6190	0.293°	700	+0.6
45.72	1.0101	0.083°	711	+2.1
"	4.4898	0.365°	718	+3.2
"	8.0070	0.664°	704	+1.2

Calculated for $P_6N_6Cl_{12}$, 695.8.

Hexaphosphonitrilic chloride fuses at 91° (corr.), and boils at 261°–263° (corr.) at 13 mm., and at 281°–282° (corr.) at 26 mm. It may be recrystallized from benzene, in which, however, it is more soluble than triphosphonitrilic chloride; ether, gasoline, and carbon disulphide also dissolve it readily; in alcohol it dissolves somewhat slowly with decomposition. It shows no tendency to superfusion. It crystallizes well, in rather large crystals, which were examined by Mr. Wirt Tassin, to whom I am indebted for the following statement:

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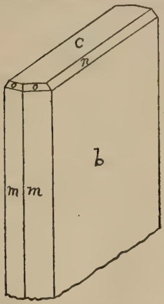
[1] A contamination with $P_6N_7Cl_9$ may be detected by treatment with gasoline, when the much smaller crystals of the latter are seen to dissolve much more slowly.

" $P_6N_6Cl_{12}$ crystallizes in the orthorhombic system in long, prismatic crystals, showing the following forms: *c* (001), *b* (010), *m* (110), *o* (111), *n* (011). Of these *c* is the dominant form; *b* large and well developed; *m* fair, though usually narrow, and *o* and *n* small and usually in similar development. *c*, *b*, *m*, *o* is the combination occurring most frequently; less often *c*, *b*, *m*, *n*, *o*; and rarely *c*, *b*, *m*. Angles *m* : *m* 57° 28′, *b* : *m* 61° 16′, *b* : *n* 40° 23′, *n* : *c* 49° 37′. Axial ratio $a : b : c =$ 0.54824 : 1 : 1.17568. The crystals are optically positive. Plane of the optic axes (100); colorless to white; transparent; and have a perfect basal cleavage."



It is scarcely attacked by boiling water, but if kept in moist air it very slowly evolves hydrochloric acid. Its ether solution, shaken with water, slowly gives a metaphosphimic acid; syrupy chlorhydrines are formed as intermediate products.

Heptaphosphonitrilic Chloride, $P_7N_7Cl_{14}$.—After many distillations, this gave:

	Calculated for $P_7N_7Cl_{14}$.	Found.
P	26.75	26.57
N	12.11	12.12
Cl	61.14	61.28

Ratio P : N : Cl = 1 : 1.01 : 2.02.

Molecular Weight. Solvent: Benzene.

Grams solvent.	Grams substance.	Elevation.	Molecular weight.	Percentage variation from theoretical.
47.09	3.5621	0.250°	808	—0.5
"	7.3979	0.523°	802	—1.2

Calculated for $P_7N_7Cl_{14}$, 811.7.

Heptaphosphonitrilic chloride is a nearly colorless, rather viscous liquid, which does not solidify at — 18°, and which boils at 289°–294° (corr.) at 13 mm., undergoing some polymerization. It is readily miscible with benzene, gasoline and ether, and towards water shows the stability manifested by the preceding chloronitrides.

Residual Oily Phosphonitrilic Chlorides.[1]—The residue which did not distil at 13 mm. when the temperature of the bath was 370°, was boiled with water to remove the solid polyphosphonitrilic chloride, filtered, and carefully dried *in vacuo* over sulphuric acid. It is a thick liquid which gave on analysis:

	Calculated for $(PNCl_2)_x$.	Found.
P	26.75	26.79
N	12.11	12.39
Cl	61.14	62.00

Ratio, P : N : Cl = 1 : 1.02 : 2.02.

Although the oil is doubtless a mixture, the above figures show that the constituents are members of the series $(PNCl_2)_n$. A determination of *the mean molecular weight* was made, with the following results:

Grams solvent.	Grams substance.	Elevation.	Molecular weight.
46.72	4.130	0.178°	1326
"	7.853	0.348°	1290

Mean 1308. This does not lie far from that required by the formula $P_{11}N_{11}Cl_{22}$ (calculated, 1276). This result is interesting in as far as it shows that a phosphonitrilic chloride of this molecular weight may exist, that it is stable and miscible with benzene, gasoline and ether, and that the molecular weight of the solid polymer described below, which is insoluble, is probably very much higher. The oil has a reddish brown color, due to dissolved impurities, which are destroyed by heating with strong nitric acid. It cannot be distilled even at 13 mm., as it polymerizes almost instantly. In its behavior towards water, it resembles the preceding members of the series.

Polyphosphonitrilic Chloride, $(PNCl_2)_x$.—This remarkable body, frequently alluded to above, is formed when any of the lower members are heated, slowly at 250°, and very rapidly at 350°. As the change is reversible, *complete* transformation cannot be effected, but reaches perhaps 90 per cent., the remainder consisting not only of the original phosphonitrilic chloride, but of others. These can be extracted by anhydrous benzene. The sample, the analysis of which is given, was prepared by heating pure triphosphonitrilic chloride in a sealed tube at 350°–360°. The transparent elastic product was repeatedly extracted with benzene dried over sodium and the absorbed benzene removed in a vacuum with constant exhaustion over paraffin, and finally by heating *in vacuo* at 110°. Analysis gave:

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[1] It is unlikely that these consist entirely of the original depolymerization products; a portion is doubtless formed by polymerization during distillation.

	Calculated for $(PNCl_2)x$.	Found.
P	26.75	26.78
N	12.11	12.27
Cl	61.14	60.45

Ratio, P : N : Cl = 1 : 1.01 : 1.98.

Polyphosphonitrilic chloride, when perfectly pure, is colorless and transparent, but is generally somewhat discolored by traces of organic matter. Its most striking property is its elasticity. It may be drawn out like rubber, and shows even a greater tendency to rebound from hard surfaces. It is readily cut with the shears. It is insoluble in all neutral solvents, but absorbs benzene, swelling to many times its original volume and forming a jelly of but little coherence; on evaporating the benzene it returns to its original condition; ether is absorbed, but less readily, and other chloronitrides are taken up in a similar manner. Hot water slowly dissolves it with decomposition; in warm dilute ammonia it swells, gelatinizes and finally dissolves; hot caustic soda does not dissolve it readily, apparently insoluble sodium salts being formed. It begins to depolymerize towards 350°, and this change is rapid just below red heat, and is accompanied by partial fusion, the products being, as described above, a mixture of lower phosphonitrilic chlorides. These transformations are not modified by heating in an atmosphere of hydrochloric acid. When perfectly pure, it leaves no residue whatever on distilling. No difference could be detected in the product formed from different phosphonitrilic chlorides.

Nitrilo-hexaphosphonitrilic Chloride, $P_6N_7Cl_9$.—The separation of this chloronitride, which does not belong to the phosphonitrilic chloride series, is described above. After four crystallizations from benzene, it gave:

	Calculated for $P_6N_7Cl_9$.	Found.
P	30.84	30.74
N	16.29	16.29
Cl	52.87	53.01

A molecular weight determination, kindly made for me by Dr. H. C. Jones, of the Johns Hopkins University, with a limited quantity of material, in benzene solution, gave 667; calculated for $P_6N_7Cl_9$, 603.5. This, with the analysis, suffices to establish the above molecular formula.

Nitrilo-hexaphosphonitrilic chloride strikingly resembles the phosphonitrilic chlorides. It fuses at 237°.5 (corr.) and boils at 251°–261° (corr.) at 13 mm. without change. The boiling-point coincides closely with that of hexaphosphonitrilic chloride (261°–263° corr. at 13 mm.), hence it is found associated with the latter. Heated in small quantities on foil, it volatilizes without residue, but at a higher temperature in a sealed tube it undergoes a change the exact nature of which has not been determined, but which involves the formation of a substance resembling polyphosphonitrilic chloride, which yields lower phosphonitrilic chlorides on distilling. It crystallizes in transparent prisms of not more than 1 mm. in length, apparently rhombic, which are often united to acicular forms. When pulverized it becomes electrified. It dissolves in about 20 parts cold and 5 parts boiling benzene,[1] is more soluble in carbon disulphide, but less soluble in gasoline and in ether. Towards water it is nearly as stable as hexaphosphonitrilic chloride, but is slowly attacked when exposed to atmospheric moisture. Hot dilute ammonia dissolves it very slowly, but more rapidly when alcohol is added.

This body is obviously a secondary product of the reaction of phosphorus pentachloride and ammonium chloride, as it is never found when a pure phosphonitrilic chloride is polymerized and depolymerized. It is noteworthy that no indication of other bodies of a similar nature has been observed, although no reason appears why they should not be formed at the same time. Whether it is in reality hexaphosphonitrilic chloride in which three chlorine atoms are replaced by one of nitrogen or not, cannot be decided at present.

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[1] Approximate only.

U. S. GEOLOGICAL SURVEY, WASHINGTON, D. C.,
JULY, 1897.

Contributions from the Chemical Laboratory of the Case School of Applied Science.

XXVIII.—PRELIMINARY PAPER ON THE COMPOSITION OF CALIFORNIA PETROLEUM.

BY CHARLES F. MABERY.

During the last four years I have been extremely desirous of undertaking an examination of California petroleum, and have made several attempts to procure specimens of the crude oil. But all attempts to procure authentic material failed for a long time, and my time was so fully occupied with oils from other fields, with an adequate supply at hand, that I could scarcely have found time to devote to it. Last February Professor Peckham informed me that he hoped to make arrangements to continue his study of the California products in the direction of determining their composition. Although I had then recently been informed that a quantity of crude oil from the Ventura County field had been shipped to me, I gladly offered Professor Peckham any facilities in my laboratory he might need for prosecuting this work. Subsequently I learned that a change in his plans would not permit of his carrying out his intention, and he informed me that I was at liberty to proceed on my own plans. Having received another specimen of crude oil from Fresno County I undertook the work with vigor. While there is still much to be done on the higher vacuum distillates, it has seemed best at this stage to give an account of what has been accomplished.

In the extremely interesting account which Peckham gave in "The Production of Petroleum" by the late Joseph D. Weeks in 1894, of the occurrence and technology of California petroleum, it appears that the production of crude oil in 1894 from all sources amounted to 683,000 barrels. On account of the peculiar occurrence of oil in these fields, and the properties of the crude oils, which differ within very wide limits between the most volatile Pennsylvania crude oil, and the heaviest products next to asphalt, these oils possess an extreme interest not inferior to that of any American petroleum. I hope to include in this examination a sufficient range of crude oils from different fields to be able to demonstrate the composition of the typical specimens.

The oils I have received are so different in their properties that they may be accepted as extremes in a series of widely varying products. One specimen from Ventura County is extremely heavy, small proportions distilling below 150°; the other from Fresno County is much lighter, and it distils in very large proportions below 150°, leaving comparatively small amounts above 250°.

Ventura County Petroleum.

The peculiar occurrence of oil in the Ventura County field where it is found in the strata of shales at shallow depths, never greater than 117 feet, or in places as the heavier maltha, has been fully described by Peckham, and accounts of these products are also given by Redwood and other authors of works on petroleum. The specimen which I received was very thick and dark, nearly black, slightly brownish in transmitted light. A determination of its specific gravity at 20° gave 0.8882. It is a high sulphur oil, as shown by a combustion which gave 0.84 per cent. It is also one of the California oils which contain a high percentage of nitrogen compounds; a determination by the Kjeldahl method gave 0.53 per cent. It showed a larger capacity for the absorption of bromine than Pennsylvania or Ohio oils, but approximately the same as that of Canadian oil from Oil Springs. Its bromine-absorption was found to be 17.72 per cent. It is quite probable that a considerable proportion of the bromine disappeared by substitution, since evidently the crude oil contains large quantities of the aromatic hydrocarbons. A combustion of the crude oil gave 85.60 per cent. of carbon, and 12.84 per cent. of hydrogen. The proportion of oxygen compounds would therefore seem to be quite small.

A distillation of the crude oil under atmospheric pressure gave 9.7 per cent. below 150°, 29.1 per cent. between 150° and 300°, and 61.2 per cent. of residue above 300°. The specific gravity and bromine-absorption of the distillates are given in the following table:

	Br-Absorption.	Specific gravity.
−150°	5.6	0.7395 at 20°.
150°–200°	6.0	0.7823 " "
206°–250°	9.17	0.8252 " "
250°–300°	18.15	0.7591 " "
−300°	....	0.9528 " 45°.

The first distillate began to appear at 60°, but small amounts came over below 150°. All portions were colorless below 250°; at this point a yellow color appeared with an odor of decomposition. The higher distillates became dark yellow on standing and gave more odor of decomposition. The residue above 300° was a thick, nearly solid, tar, and its high specific gravity with the large proportion remaining above 300° explains in part the difficulty that has been encountered in preparing burning oil from Ventura County petroleum. In the distillation under atmospheric pressure, cracking began at 350°; while the distillate above was somewhat decomposed, these higher portions appear to be quite stable.

For the separation of constituents with higher boiling-points 20 liters was distilled under atmospheric pressure to 150°, then the distillation was continued *in vacuo* under a tension of 50 mm. to 275°. The following weights were obtained within limits of 25°; the specific gravity determinations were made on a Westphal balance:

Atmospheric pressure.	Weight in grams.	Specific gravity at 20°.
−150°	850	0.7269
−100°	605	0.7342
100°–125°	1000	0.7452
125°–150°	1050	0.7689
150°–175°	1115	0.8212
175°–200°	1110	0.8432
200°–225°	1025	0.8618
225°–250°	1565	0.8824
250°–300°	1005	0.9071

The next distillation in vacuum was made within 5°, but the results of subsequent work on these portions will be presented in another paper.

None of the vacuum distillates nor the residue showed the slightest indication of decomposition; all portions had the natural odor of the constituents of the crude oil. The fraction 250°–275° when cooled with salt and ice became nearly solid from the separation of paraffin, but from the next lower fraction scarcely any paraffin separated.

To ascertain whether the series C_nH_{2n+2} forms the main body of this petroleum below 200°, distillation under atmospheric pressure of the lower portions was continued until the constituents collected within the limits of their characteristic boiling-points. After the sixth distillation 20 grams collected at 78°–84°, which was shown to contain a large proportion of benzol by the formation of nitrobenzol. The formation of nitrotoluol in the fractions 108°–112° showed the presence of toluol. Approximately 25 grams collected at 97°–100° which gave as its specific gravity 0.7341 at 20°, a value much higher than the specific gravity of the heptane from Pennsylvania petroleum, 0.7184 at 15° (Warren), but approaching the specific gravity of the distillate 95°–100° separated by Beilstein and Kurbatoff from Russian petroleum, 0.748. A portion of this distillate was agitated thoroughly with a mixture of nitric and sulphuric acids, and boiled with sodium until the nitro-product in solution was completely decomposed, and again distilled. Its specific gravity was then 0.7268, considerably higher than the specific gravity found by Warren in the corresponding distillates from Pennsylvania oil after treating with concentrated nitric acid, 0.7048, but approximately the same as Beilstein and Kurbatoff found in the Russian distillate after treating with fuming sulphuric acid, 0.733. A combustion of this fraction gave the following percentages of carbon and hydrogen:

0.1575 gram of the oil gave 0.4950 gram CO_2 and 0.1995 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.71	85.70
H	14.29	14.08

The composition was not changed by purification, an analysis giving:

C	85.60
H	14.28

The oil which separated after treatment with the mixture of acids soon became solid and partially crystallized in long, slender needles. It will be further examined. The high specific gravity of this product and the proportions of carbon and hydrogen would seem to indicate heptanaphthene.

At 117°–119°, after the seventh distillation, 35 grams collected that gave as its specific gravity, 0.7489 at 20°. The following percentages of carbon and hydrogen were obtained by analysis :

0.1568 gram of the oil gave 0.4920 gram CO_2 and 0.1958 gram H_2O.

C	85.59
H	13.87

Upon treating a portion of this distillate with nitric and sulphuric acids a light yellow oil heavier than water separated that was doubtless nitroxylol. The remaining oil was boiled a long time with sodium, agitated with fuming sulphuric acid, washed with sodic hydrate, dried and again distilled. Analysis of the purified oil gave the following results :

0.1606 gram of the oil gave 0.5037 gram CO_2 and 0.1996 gram H_2O.

	Calculated for		
	C_nH_{2n}.	C_nH_{2n+2}.	Found.
C	85.71	84.20	85.55
H	14.29	15.79	13.81

Specific gravity of the purified oil, 0.7405. Even after the vigorous means of purification to which this distillate was subjected it showed no change in its composition. The specific gravity of petroleum octane boiling at 119.°5, is 0.7100 ; of octonaphthene which Beilstein and Kurbatoff separated from Russian oil, after purification with nitric and sulphuric acids, 0.7582 at 17.°5.

The high specific gravity, and the proportions of carbon and hydrogen, suggest the possibility that this body from the California oil may be octonaphthene.

45 grams of an oil collected at 123°–125°, that gave as its specific gravity at 20°, 0.7553. The following composition was shown by analysis :

0.1574 gram of the oil gave 0.4935 gram CO_2, and 0.1975 gram H_2O.

C	85.49
H	13.91

After thorough treatment with nitric and sulphuric acids and boiling with sodium, the specific gravity of this oil was reduced to 0.7424, and a combustion gave the following percentages of carbon and hydrogen :

0.1507 gram of the oil gave 0.4720 gram CO_2, and 0.1946 gram H_2O.

	Calculated for		
	C_8H_{18}.	CnH2n.	Found.
C	84.20	85.71	85.43
H	15.79	14.28	14.33

These values are sufficient to exclude normal octane in any considerable quantity from this oil. If this hydrocarbon is not present, further distillation should separate this fraction into lower and higher constituents.

No further attention was given to the portions between 125° and 155°. At 159°–160°, after the eleventh distillation 30 grams came together, which gave as its specific gravity 0.7898. A combustion gave the following percentages of carbon and hydrogen :

0.1680 gram of the oil gave 0.5257 gram CO_2, and 0.2109 gram H_2O.

C	85.35
H	13.95

After treatment with the acid mixture and sodium the composition was scarcely changed.

0.1652 gram of the oil gave 0.5174 gram CO_2, and 0.2086 gram H_2O.

	Calculated for CnH2n.	Found.
C	85.71	85.40
H	14.29	14.04

Markownikoff found the specific gravity of dekanaphthene, boiling-point, 160–165, to be 0.783 at 15°.

At the end of the seventeenth distillation, 50 grams collected at 169°–172°, with a specific gravity 0.7987 at 20°. A combustion gave the following percentages of carbon and hydrogen :

0.1614 gram of the oil gave 0.5051 gram CO_2 and 0.2046 gram H_2O.

C	85.35
H	14.09

Agitation of this fraction with the acid mixture caused the separation of a nitro-product heavier than water. It required long continued action of sodium to remove entirely the nitro-derivative. After redistillation the remaining oil was unchanged on long standing with sodium. Its composition was hardly changed by the action of the acids.

0.1670 gram of the oil gave 0.5090 gram CO_2, and 0.2046 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.71	85.69
H	14.29	14.21

A determination of the specific gravity of the purified oil at 20° gave 0.7733.

The distillation of the higher portions was not carried far enough for a separation of their individual constituents.

The presence in this petroleum of a constituent with a boiling-point in the vicinity of 170°, the boiling-point of the decane in Pennsylvania petroleum, is a peculiar coincidence. After seventeen distillations it would seem that any mixture should separate into its constituents. (In the vicinity of 180° very little distillate collected. The treatment with acids should have been sufficient to remove the cymols.)

The high specific gravity of the distillates 97°–100°, 117°–119°, 159°–160°, 169°–170°, with the percentage composition supporting the series C_nH_{2n}, indicates the naphthenes. These bodies evidently require further study.

Fresno County Petroleum.

As explained above, this oil differs very materially in its properties from the Ventura County product. It is lighter in color and has more of a greenish hue. Its lower specific gravity at 20°, 0.8423 indicates more of the volatile constituents. A combustion gave the following percentages of carbon and hydrogen: Carbon, 86.24; hydrogen, 13.08. It is not a high sulphur oil, as shown by a combustion, which gave 0.21 per cent. of sulphur. A determination of sulphur by the

Kjeldahl method gave I, 0.10; II, 0.12 per cent. The bromine-absorption of the crude oil gave 9.07 per cent., considerably less than that of the Ventura County oil.

Under atmospheric pressure this oil distilled in the following proportions:

	Per cent.
−150°	33.06
150°–200°	24.79
200°–250°	20.66
250°–300°	12.40
Residue	9.09

All these distillates were colorless below 250°. Determinations of bromine-absorption and specific gravity gave the following results:

	Bromine-absorption.	Specific gravity at 20°.
−150°	17.21	0.7829
150°–200°	14.23	0.8268
200°–250°	32.10	0.8725
250°–300°	21.68	0.9090
+300°		0.9356

The absorption of bromine by these fractions is very much greater than by the corresponding fractions from Ventura County oil. This cannot be due to cracking, since, although the difference is greater in the distillate 200°–250°, it is large in the distillate below 150°. Similar differences are observed in the specific gravity of the distillates; those from the Fresno County oil are much higher than those from the Ventura oil.

When distilled *in vacuo*, 10 liters of the Fresno County oil gave the following weights:

	Weight in grams.
−150° (at. pres.)	2090
−100° (50 mm.)	1165
100°–125°	970
125°–150°	1445
150°–175°	935
175°–200°	595
200°–225°	330
Residue	2470

The distillation of these fractions is now in progress within narrower limits of temperature.

Aid in the work described in this paper was given by the

American Academy of Arts and Sciences from the C. M. Warren fund for chemical research. I have been aided in the experimental details by Mr. P. M. Shaw, who selected a portion of this work as the subject of a thesis for the degree of Bachelor of Science, and by Mr. Edward J. Hudson, who will continue with me the study of California petroleum.

ON THE SOLUBILITY OF AMMONIA IN WATER AT TEMPERATURES BELOW 0° C.

BY J. W. MALLET.

Roscoe and Dittmar's table[1] of the solubility of ammonia in water at different temperatures, under normal pressure, begins at 0° C., and there seem to be no recorded measurements of solubility at any lower temperatures. It is stated on the authority of Fourcroy and Vanquelin[2] that a "concentrated" aqueous solution of ammonia—the exact amount in solution not given; probably not determined—does not freeze till cooled to between —38° and —41°, that it then forms brilliant flexible needles, and that at —49° it solidifies to a gray gelatinous mass, almost destitute of odor.

It seemed interesting to try the effect of continuing to pass gaseous ammonia into an already strong aqueous solution at temperatures much below zero, and particularly to see whether any visible change of behavior would mark the presence of enough ammonia to represent the hydroxide of ammonium, often assumed to exist in the ordinary solution, but without any surplus water. The proportion in question—one molecule of ammonia for one of water, might, from an inspection of Roscoe and Dittmar's table, be expected to occur at a temperature but little below zero. Taking advantage of a fall of finely pulverulent dry snow, followed by two or three days of cold weather, during which the atmospheric temperature was about —8° to —12° C., the following experiments were made last winter. In anticipation of such an opportunity, the apparatus had been made ready some time before.

A strong solution of ammonia in water was placed in a burette-like glass tube of the form shown in Fig. 1, of which the larger cylindrical part was about 220 mm. long and 25 mm. in internal diameter, the narrow tube below about 100 mm. long and only about 1 mm. in internal diameter, with a small glass stop-cock about 30 mm. above the orifice. The cylinder was graduated for about two-thirds of its length into cubic centimeters. By means of an india-rubber stopper, perforated to grasp tightly the narrow tube, and then cut in two in the line of its axis, this part of the burette was fixed in the neck of an inverted gas-jar, the body of which was about 180 mm. high, with an internal diameter of about 120 mm., so that the cylindrical body of the burette could be surrounded by a freezing-mixture contained in the jar, without any leakage occurring at the neck, the narrow—almost capillary—tube and stop-cock being below and outside the jar. The open mouth of the burette above was loosely closed by a doubly-perforated stopper, through which passed a small tube for the introduction of ammonia gas, and an alcohol thermometer, each fitting so as to be easily slid up or down. The thermometer was carefully made by Mr. Henry J. Green, of Brooklyn, N. Y., contained pure (uncolored) alcohol, was graduated on the glass stem, and had the (centigrade) scale verified by comparison with a (Fahrenheit) mercurial thermometer, itself tested by comparison with a gas thermometer, at the following points; +32°, +12°, —8°, and —28° F. The gaseous ammonia was obtained by simply heating in a flask the strong aqueous solution. There was, of course, no need for drying it, but it was cooled, and incidentally in large measure dried, by passing it first through an empty flask surrounded by snow, and then through a spiral coil of glass tubing immersed in a bath of snow and common salt. Thence by an india-rubber connecting tube it passed into the already strong solution in water contained in the burette. This was surrounded in the jar by a freezing-mixture of snow and commercial hydrochloric acid, both materials having been separately cooled down in advance by snow and salt. In consequence of the evolution of heat as more ammonia was absorbed by the water in the

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[1] J. Chem. Soc., **12**, 128—quoted in Roscoe and Schorlemmer's Treatise on Chemistry, **1**, 385.

[2] L. Gmelin's Handbook of Chemistry (Cavendish Soc. transl.) **2**, 425.

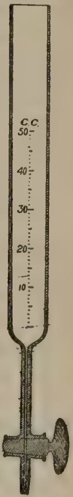


Fig. 1.

burette, it became necessary to allow ample time for cooling down again, and to renew the freezing-mixture in the jar, drawing off the old mixture by means of a specially arranged and rapidly acting siphon. In order to get the lowest temperature reached (between —45° and —46° C.) it was necessary to doubly cool the last portions of snow and hydrochloric acid, first by snow and salt, and then by separate exposure to some of the already cooled snow and hydrochloric acid mixture. The passage of the gas into the solution was continued until it went through very freely unabsorbed. The liquid in the burette continually increased in volume, so that, when samples were drawn off by the stop-cock, enough was first run off to effectually cool the projecting part of the narrow tube and the stop-cock itself, and to bring the level of the remaining liquid down to one of the graduation marks, from which a measured sample might then be taken off. A number of light glass flasks, each of about 300 cc. capacity, furnished with stoppers, were in advance about three-fourths filled with water and severally weighed with accuracy on a good analytical balance. These flasks of water were brought down to 0° C. by immersion in snow, and—operating out of doors—the several samples of liquid ammonia were run into them from the burette, producing at once such large dilution that there was no further fear of loss of ammonia by standing over, with the stoppers inserted, until the flasks could be reweighed—the gain of weight in each case representing the amount of liquid taken from the burette—and the amount of real ammonia determined by neutralization with a standard solution of sulphuric acid. The first sample was taken at —40° C., and then, by simply removing the freezing-mixture of snow and hydrochloric acid from the jar, the temperature of the liquid in the burette was allowed to slowly rise, and as the thermometer marked different desired points it was raised for a moment out of the liquid, another sample drawn off into the water in one of the flasks beneath, and the thermometer lowered again. One or two fairly good measurements of the volumes of the samples were made, but, owing to the necessity for quick work, and the difficulty of seeing satisfactorily through the dimmed surface of the glass, most of these measurements were little to be relied on.

The following results were obtained, so expressed as to form a continuation of Roscoe and Dittmar's table. The atmospheric pressure at the time was 743–744.5 mm., corrected for temperature of the mercurial column.

At —10° C. 1 gram of water dissolved 1.115 grams of ammonia.

At —20° C. 1 gram of water dissolved 1.768 grams of ammonia.

At —30° C. 1 gram of water dissolved 2.781 grams of ammonia.

At —40° C. 1 gram of water dissolved 2.946 grams of ammonia.

The taking up of enough ammonia to form ammonium hydroxide was not attended with any apparent change of behavior, and continuous liquefaction went on smoothly to the lowest temperature reached, with no separation of any solid product. After the freezing-mixture had been withdrawn the temperature rose at first very gradually in consequence of rapid surface evaporation of ammonia. At —25° C. (barometer at 743.4 mm. (corr.)) steady, but not tumultuous ebullition took place and continued for several minutes. A sample taken at this point had the composition : 1 gram of water and 2.554 grams of ammonia.

By interpolation from Regnault's results, the tension of the vapor from liquefied ammonia at —25°.6 C. would be about 1167 mm.

A sample was also taken at —3°.9, which proved to consist of 1 gram of water and 0.947 gram of ammonia—this last corresponding almost exactly with the calculated proportion for ammonium hydroxide, and agreeing also quite closely with an extension of Roscoe and Dittmar's table to the temperature named, allowance being made for the pressure being a little below normal.

These results are graphically plotted in Fig. 2, which includes also the determinations of Roscoe and Dittmar for +40° to 0°. It will be seen that the curve changes rapidly a little below the temperature corresponding to the formation of

$(NH_4)OH$, and the amount of ammonia absorbed is much

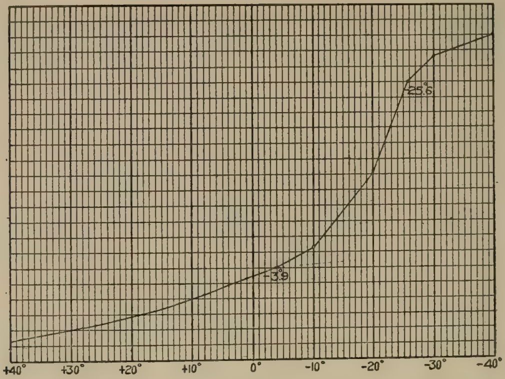


Fig. 2.

greater than would be called for by an extension of Roscoe and Dittmar's numbers.

As regards the reversal of curvature before —30° is reached, some allowance must doubtless be made for loss of ammonia by the samples drawn at the lowest temperatures in dropping through the air into the ice-water in the flasks in spite of the precautions taken to minimize loss from this source. And, in view of the fact that liquefied ammonia boils at —33°.7 under a pressure of 749.3 mm. (Bunsen), the amount of ammonia found in the contents of the burette below this point would, of course, go on increasing indefinitely, depending simply on the length of time allowed for condensation and the more or less free supply of the gas. It appears that ammonium hydroxide, if such a substance exist, or the solution of ammonia in water in proportion corresponding to such a compound, continues to dissolve gaseous ammonia, or mixes with liquefied ammonia, down to and beyond the normal boiling-point of the latter, but the proportion dissolved is much greater than would be called for by an extension of the curve representing solubility at temperatures above 0°.

As has been stated, measurement of the volumes of the samples taken could not be very satisfactorily carried out. It may be mentioned, however, that a comparison of volume with weight gave for the liquid at —30° a density of about 0.718, and for that at —40° about 0.731, as referred to water at +4°. The latter figure being greater than the former may probably be accounted for by the very high value of the coefficient of dilatation for liquefied gases. Calculating from Jolly's results, the density of liquefied ammonia itself at —40° ought to be something like 0.673.

UNIVERSITY OF VIRGINIA,
August 30, 1897.

NOTE ON A SOMEWHAT REMARKABLE CASE OF THE RAPID POLYMERIZATION OF CHLORAL.

BY J. W. MALLET.

A specimen of anhydrous chloral—trichloracetaldehyde—of about 250 grams was contained in a glass vial of a form commonly used in Germany, with small drawn-out neck, hermetically sealed. It had been on hand for more than a year, and had originally been quite clear, but doubtless not absolutely pure, very likely containing traces of sulphuric acid, as a few small white flocks of the polymeric meta-chloral had begun to show at the bottom.

This specimen, with a number of others, had been exhibited on the lecture-table, handled by several persons, and moved back to the collection room whence it had come. It was placed temporarily on a table, among other bottles, in the afternoon, to be next morning restored to its place in the collection on the shelves. No one went into this room, which is in a locked portion of the building, before the following day. The temperature was moderate—about 20° or 22° C.—and differed but little from that of the lecture room. The place on the table occupied by the bottles did not receive any direct rays of the sun.

On coming into the room in the morning, a strong odor of chloral at once drew attention to the table, where a circle of half a meter or so in diameter was covered with a thin crust of white meta-chloral. The remains of the sealed vial were found as small fragments scattered about the room, some of them as much as two or two and a half meters away from where the vial had stood, and some of them on the shelves at a higher level than the top of the table, showing clearly that the vial had not fallen down, or been knocked over by a mouse or rat, but had burst, and with some considerable force, although no other bottle standing near it had been broken.

It seems that polymerization must have taken place so rapidly, and to so large an extent that the heat evolved in the unison of the smaller into larger molecules raised the temperature of the remaining liquid chloral to a point at which the tension of its vapor was more than the vial could withstand.

If this explanation be accepted, the occurrence is in three respects noteworthy. In the first place, the amount of heat evolved in the polymeric change must have been quite large to produce the effect observed, remembering that liquid chloral is only about as volatile as water—has about the same boiling-point under atmospheric pressure ; I do not know of any recorded measurements of the thermal value of the change in question. Secondly, the polymeric change must have occurred with a degree of suddenness which is surprising in view of the very gradual transition from liquid chloral to meta-chloral which is usually observed—other specimens, prepared in this laboratory, have taken several years to become entirely solid. Thirdly, it is not easy to imagine what cause can have provoked this sudden polymerization, there having been less mechanical agitation, less change of temperature, less external disturbance of any kind that can be pointed out, at the time when the change occurred than the specimen had previously been exposed to.

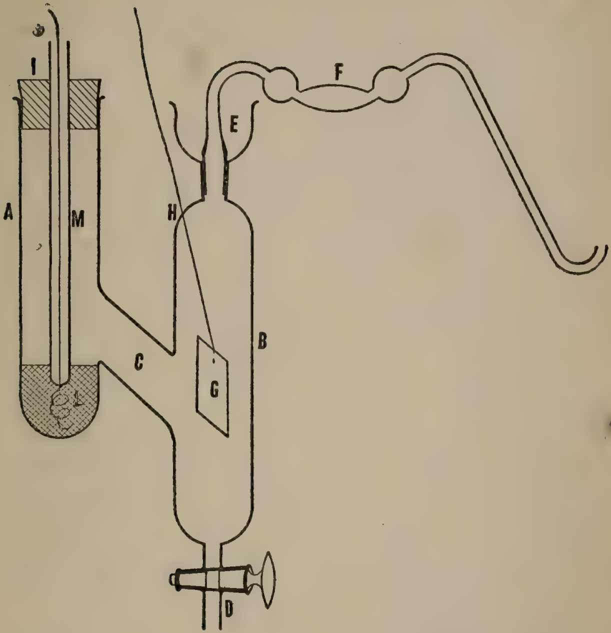
University of Virginia,
August 27, 1897.

A NEW FORM OF HYDROGEN GENERATOR.

By E. W. Magruder.

Several difficulties have been experienced in using Bunsen's hydrogen generator, to overcome which the following apparatus has been devised.

The apparatus (see figure) consists of a tube *A*, closed at the bottom, and connected by means of the inclined side tube



C with the tube *B*, which is furnished at the bottom with the stop-cock *D*, and at the top with the funnel *E*, into which fits with a ground joint the delivery-tube *F*. Tube *B* also contains the platinum electrode *G*, opposite the side tube, suspended by a platinum wire fused through the tube at *H*. Zinc amalgam is put into *A* until it nearly reaches the tube *C*. *A* is closed with a rubber stopper *I* carrying a glass tube *M* containing a platinum wire fused through the tube at *L*. The wire dips into the amalgam. The apparatus may be simplified by leaving off the stop-cock *D*, and by fusing the delivery-tube *F* directly to the top of *B*. The apparatus thus made would be cheaper and for many purposes equally good.

The apparatus is suspended in a battery-jar, filled with water, by means of a wooden block which clamps the apparatus at the top and rests at the top of the jar.

The objections to the Bunsen form are the following: (1), the uncertainty of obtaining hydrogen free from oxygen, for if oxygen escapes from the amalgam it must of necessity mix with the hydrogen; (2), if the zinc is impure, and volatile hydrogen compounds should be formed, they will mix with the hydrogen; (3), the clogging of the apparatus caused by the formation of zinc sulphate which remains at the bottom covering the amalgam and thus preventing fresh acid from coming in contact with the zinc.

The first and second objections are overcome by having the oxygen and hydrogen electrodes in separate tubes; if oxygen or any other gas escapes it simply rises to the surface in tube *A* and does no harm, as it cannot mix with the hydrogen in *B* without first passing down the side tube *C*, a path which it is hardly likely to follow.

The third objection is overcome by having the amalgam nearly up to the side tube, down which the zinc sulphate flows as soon as formed into *B*, from which it can be drawn off through the stop-cock. This adds greatly to the ease of cleaning the apparatus.

Tests made with the gas generated showed that it is perfectly pure hydrogen.

The apparatus can be obtained from Mr. Emil Greiner, of New York.

Chemical Laboratory, Johns Hopkins University,
June, 1897.

NOTES.

VICTOR MEYER.

The distinguished Professor of Chemistry in the University of Heidelberg, Germany, died suddenly on the 8th of August. Victor Meyer was born on the 8th of September, 1848, in Berlin. At the age of sixteen he entered the University of Berlin after having completed a preliminary course of study in a "Gymnasium." After one semester at Berlin he went to Heidelberg to work under Bunsen, whose successor he became in later years. He received his degree from the University of Heidelberg, and then returned to Berlin to continue his studies under Von Baeyer. In 1871 he was called to Stuttgart as first assistant to Von Fehling at the Polytechnic Institute, and was given the title of Professor of Organic and Theoretical Chemistry. A year later he was appointed Professor of General Chemistry in the Polytechnic Institute of Zurich. Here he remained for twelve years. In 1885 he succeeded Hübner as Professor of Chemistry at Göttingen, and four years later he was called to Heidelberg.

He was one of the most active and brilliant chemists of his time, and he was most successful in his work. Probably no other chemist has done more to enlarge the boundaries of chemistry and to clear up dark places during the past quarter of a century than Meyer. Among the many important investigations carried out by him and his students, the following may be mentioned: When he began his career there was a good deal of confusion in the classification of the di-derivatives of benzene. By the application of a reaction devised by him—the fusion of a sulphonate with an alkali formate—he was able to show that salicylic acid, which had been regarded as a meta compound, belongs in reality to the ortho series. This led to important consequences. Shortly afterward he brought to light and thoroughly examined the aliphatic nitro compounds. In the course of this work he discovered the isonitroso compounds, and showed that they are oximes. The study of the oximes led to their preparation by the treatment of aldehydes and ketones with hydroxylamine, and the foundations of the stereochemistry of nitrogen compounds were thus laid. He devised a simple method for the determination of vapor densities—a method that has come into general use. In the application of this method he showed that when the vapor of iodine is heated to a high temperature its density becomes less and less until finally it is such as to show that the iodine molecules have been split into two atoms each. At least that is the simplest conclusion to be drawn from the facts established. He discovered thiophene in benzene, and worked out its chemistry and that of its homologues and derivatives in a marvelously perfect way. Thiophene is, in fact, said to be one of the most thoroughly studied substances.

Within the last few years he has been engaged in the investigation of the iodoso compounds and the iodonium bases, both of which classes of substances awakened the interest of chemists to an unusual degree. The "Lehrbuch der organischen Chemie," written by himself and Jacobson, is the most interesting and valuable text-book of this subject now available.

It is generally stated that the indirect cause of his death was over-work. He had been warned repeatedly to spare himself, but his inborn desire for activity seems to have been uncontrollable.

PAUL SCHÜTZENBERGER.

M. Paul Schützenberger died in Paris, June 28th, 1897. He was born in Strasbourg, Dec. 23rd, 1829, and received his doctorate from that university at the age of twenty-six. He turned his energies to chemistry, and was appointed to that chair in the high school ot Mühlhausen. Later he became sub-director of the chemical laboratory at the Sorbonne, and in July, 1876, was called to the leadership of chemistry at the Collége de France. He became a member of the Academy of Medicine in 1884, and in 1888 was accorded the distinguished honor of membership in the Paris Academy of Sciences, having been elected to the position made vacant by the death of M. Débray. M. Schützenberger has written a number of books, the best known being: Chimie appliquée à la Physiologie Animale et au Diagnostic Médical (1864); Des Matières Colorantes (1866); Les Fermentations (1875), which has been translated into English and published in the International Science Series; and Traité de Chimie Générale (1879). He has published also a large number of papers describing his researches on vegetable alkaloids, the constitution of the albumins, and on various inorganic substances.

Chemistry has lost from her ranks, in M. Schützenberger, one of her most active workers. H. C. J.

C. REMIGIUS FRESENIUS.

The head of the well-known laboratory at Wiesbaden, Germany, died June 11, after a long life devoted to work in the field of analytical chemistry. Fresenius was born in the year 1818. After studying at Bonn he became Privatdocent in Liebig's laboratory at Giessen, in 1841. In 1845 he went to Wiesbaden, and there he remained active until his death. At first he was Professor of Chemistry at the Agricultural Institute, but in 1848 he opened an independent laboratory for instruction. His famous books on Qualitative and Quantitative Analysis and many of his contributions to analytical chemistry are well-known to chemists. His *Zeitschrift für analytische Chemie* has also served to keep his name prominently before the chemical world, and to further the interests of his chosen subject.

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DECOMPOSITION OF HEPTANE AND OCTANE AT HIGH TEMPERATURES.

BY R. A. WORSTALL[1] AND A. W. BURWELL.

The changes produced in organic compounds by destructive distillation, have not only been for many years a fruitful subject of scientific research, but have also opened up a great field of industrial chemistry. So numerous and complex are the resulting reactions that in many cases it is difficult to decide which really are the most valuable products obtained. Substances long treated as worthless by-products of these reactions are often found later to be most valuable. It was many years before coal tar was recognized as a valuable product in the manufacture of illuminating gas, but so many valuable substances have been made from it in the last two centuries that the gas might now be said to be a by-product of the tar. It is interesting to note in this connection that the first English patent concerning the dry distillation of coal, which was granted in 1681, had to do, not with the gas, but with the pitch and tar:—"A newe way of makeing pitch and tarre out of pit coale, never before found out or used by any other."

Of all the numerous by-products arising from such treatment of organic compounds upon a commercial scale, there are perhaps none of which so little is known as those which result from the manufacture of "Pintsch" gas from petroleum. The similarly formed decomposition-products of wood, shale, turf, peat, and bituminous coal have all received considerable attention, especially those of coal. In general, it may be said that the tars resulting from the destructive distillation of turf, of brown coal, and of bituminous shale consist mainly of aliphatic hydrocarbons, that from wood of phenols and their derivatives, that from bituminous coal of aromatic hydrocarbons. While these may be taken as distinguishing features of these various substances, secondary reactions greatly complicate the relations. The same elementary material by different treatment gives different results. Thus, by the action of relatively low heat upon coal we obtain a preponderance of hydrocarbons belonging to the paraffin, olefin, and acetylene groups, while, under the influence of a higher heat, the former decrease and the aromatic hydrocarbons increase.

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[1] Thesis by R. A. Worstall for the degree of B. S., Case School of Applied Science, Cleveland, Ohio.

There have been many theories proposed to account for the change of hydrocarbons at high temperatures. That advanced by Berthelot in 1866[1] has long been accepted as the most plausible. In brief, his theory is that hydrocarbons do not decompose into carbon and hydrogen under the action of heat, but form higher and more complex molecules, this change taking place continually with increasing temperature. To quote his words: "Pure carbon is in some sense a limiting state and one which can scarcely be attained under the influence of the highest temperature we can produce." He divided pyrogenic reactions into two classes:

I. "Condensation moléculaire," or the direct combination of molecules with hydrogen or with each other.

II. "Décomposition inverse," or the breaking up of the hydrocarbon into a lower molecule and free hydrogen.

He maintained that a certain "equilibrium" exists between these two classes of reactions, which depends upon the temperature and upon the nature of the bodies acted upon, and that these two oppositely directed reactions take place simultaneously and mutually limit each other. According to his theory, the decomposition of methane would be explained by the following reactions :

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[1] Ann. Chim. Phys. [4], 9, 469.

$$\begin{aligned} 2CH_4 &= C_2H_4 + 2H_2, \\ 2CH_4 &= C_2H_2 + 3H_2, \\ C_2H_4 &= C_2H_2 + H_2, \\ C_2H_2 + H_2 &= C_2H_4, \\ C_2H_4 + H_2 &= C_2H_6, \\ 2C_2H_6 &= 2CH_4 + C_2H_2 + H_2, \text{ etc.} \end{aligned}$$

He explained the formation of aromatic hydrocarbons by the polymerization of acetylene :

$$3C_2H_2 = C_6H_6, \text{ etc.}$$

Jacobsen,[1] after investigating the subject, came to similar conclusions. To explain the formation of aromatic hydrocarbons from acetylene and allylene he proposed the following equations :

$$\begin{aligned} 3C_2H_2 &= C_6H_6, \text{ benzol,} \\ 2C_2H_2 + C_3H_4 &= C_7H_8, \text{ toluol,} \\ C_2H_2 + 3C_3H_4 &= C_8H_{10}, \text{ xylol,} \\ 3C_3H_4 &= C_9H_{12}, \text{ mesitylene.} \end{aligned}$$

Jacobsen did not believe that hydrogen was liberated by these reactions, but Anschütz[2] points out that, according to Jacobsen's theory, other hydrocarbons commonly occurring in such decomposition-products can be explained only by assuming that hydrogen is split off. Thus :

$$\begin{aligned} 5C_2H_2 &= C_{10}H_8, \text{ naphthalene, } + H_2, \\ \text{or} \begin{cases} C_{10}H_8 + 2C_2H_2 \\ 2C_7H_8 \end{cases} &\begin{aligned} &= C_{14}H_{10}, \text{ anthracene, } + H_2, \\ &= C_{14}H_{10}, \text{ anthracene, } + 3H_2. \end{aligned} \end{aligned}$$

R. D. Schulze[3] explains the formation of hydrocarbons found in coal tar by assuming that the phenols are the primary products, and that the hydrocarbons are formed from these by the splitting off of the elements of water. But Lunge points out that, considering the fact that the phenols are more stable than the hydrocarbons under the influence of heat, this theory seems scarcely plausible.

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[1] Ber. d. chem. Ges., **10**, 853.

[2] Ber. d. chem. Ges., **11**, 1215.

[3] Ann. Chem. (Liebig), **227**, 143.

Lewes[1] essentially follows Berthelot's theory. According to Lewes the decomposition of ethylene would be explained by the following reactions :

$$3C_2H_4 = 2C_2H_2 + 2CH_4,$$
$$2CH_4 = C_2H_2 + 3H_2.$$

Haber,[2] however, takes exception to all former theories. From the results of the exceedingly interesting and important experiments he and Oechelhäuser performed, with hexane and trimethylethylene, mentioned elsewhere, he arrived at the following conclusions: When aliphatic hydrocarbons with more than two carbon atoms in the molecule are heated for some time to between 600° and 800° C. they break up into lower molecules, but free carbon and hydrogen are *never* formed at this temperature. The hydrogen atoms at the point where the break occurs suffer transposition, while the bond between the carbon atoms at that point is broken. Thus, hexane gives methane and amylene, the smaller molecule formed being always a paraffin, the larger an olefin, and the latter, by polymerization, gives more complex molecules. As the paraffins containing but one or two carbon atoms cannot thus decompose without liberating carbon and hydrogen, he placed them in a special class, and condemns Berthelot's work, which was done upon just such hydrocarbons. While the formation of the doubly unsaturated and of the acetylene hydrocarbons is difficult, they are always formed to some extent.

But between 900° and 1,000° C. he found that new reactions took place and more complicated products were formed. Methane was the only paraffin, ethylene the only olefin formed at this temperature. The attraction between carbon and hydrogen weakened, and free hydrogen appeared, along with increased quantities of benzol. The latter he considered a by-product of the reaction which is not formed so long as the carbon-hydrogen attraction is stronger than that of carbon-carbon. Just how far the olefins added hydrogen cannot be said, but it was certain that ethane, propane, etc., were not formed in this way, for they did not occur in the gas. As he found benzol to be formed both from hexane and from trimethylethylene he concluded that its formation must be due to the polymerization of acetylene. He did not, however, accept Berthelot's "equilibrium," for the reactions seemed to run in different directions, and to lead to entirely different results.

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[1] Proc. Roy. Soc., **55**, 91 ; and **57**, 540.

[2] Ber. d. chem. Ges., **29**, 2691.

We thus see that while several ingenious theories of the pyrogenic reactions have been advanced, no two of them agree with each other, and, as will be seen further on, they offer at the best only a partial and unsatisfactory explanation of a few of the observed facts, while there are many features of these reactions which they do not make clear.

Historically, a consideration of the work which has been done upon the by-products of oil-gas is very interesting. Faraday was apparently the first to investigate the subject, and in 1825 he published a paper "On New Compounds of Carbon and Hydrogen, and on Certain Other Products Obtained during the Decomposition of Oil by Heat."[1] In this paper he described a new compound which he called "Bicarburet of Hydrogen," now known as "Benzol," and also another new compound, analysis of which showed carbon and hydrogen in the same proportion as in olefiant gas, but whose density was twice that of the latter. This is the composition of butylene, whose discovery has hence always been attributed to Faraday. Both of these new compounds he found in the tar from oil-gas, and his memoirs show that the gas of 1825, made from fish or vegetable oil, differs little from that of to-day, made from petroleum.

Berthelot, in 1867, was the next whose work was connected with this subject. Perhaps his most important experiments were those with acetylene.[2] By the action of relatively low heat upon acetylene enclosed in glass tubes over mercury, he obtained both solid and liquid condensation-products, among which he identified benzol, styrol, naphthalene, and hydrogen. By passing the gas through red-hot porcelain tubes he obtained considerable naphthalene, along with hydrogen, the olefins, and methane. These are among the experiments upon which he based his theory of the pyrogenic reactions, mentioned before.

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[1] Phil. Trans., 1825, 440.

[2] Ann. Chim. Phys. [4], 9, 445.

In 1877, Letny,[1] after a preliminary and doubtless incomplete investigation of the subject, came to the somewhat erroneous conclusion that the tars obtained by the dry distillation of wood and from the manufacture of oil-gas have the same composition. Continuing his work later, Letny[2] employed a petroleum residue from Baku of 0.870 specific gravity, which started to boil at 270°. He conducted the vapors of this oil through red-hot tubes 7 feet long, filled with wood charcoal. The first tar obtained went through the operation again. In this way he obtained a tar whose specific gravity was 1.027 and which was equivalent to 40 per cent, of the oil taken. He gives the composition of this tar as follows: 2.3 per cent. water; 4.6 per cent. benzol; 5.2 per cent. toluol and xylols; 26.9 per cent. naphthalene; 2.7 per cent. phenanthrene; 2.4 per cent. anthracene; 23.1 per cent. unchanged petroleum; and 20.6 per cent. pitch. These percentages doubtless represent crude products, for he makes no mention of unsaturated hydrocarbons, which are always present in these tars.

In 1878, about the same time that Letny was experimenting, Liebermann and Burg were employed upon similar work.[3] In the tars obtained by passing brown coal tar (which, as said before, consists mainly of paraffins) through red-hot tubes they identified benzol, toluol, naphthalene, and anthracene, while from a petroleum treated in the same way they obtained benzol, but scarcely any naphthalene.

Liebermann and Burg were the first to investigate the effect, upon the product obtained, of different substances when placed in the tubes. They experimented first with empty tubes, then with tubes filled with charcoal, with coke, and with pumice stone. In every case the charcoal gave the best results, while the empty tubes gave the worst. They attributed the good effects of such fillings to the greater extent of surface afforded. Letny came to a similar conclusion after comparing the results obtained by using empty tubes of different diameters, then these same tubes filled with charcoal and with platinum black. The latter gave the best results and the wide empty tubes the poorest.

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[1] Bull. Soc. Chim., 1877, 554.

[2] Ding. Jour., **229**, 353; and **231**, 190.

[3] Ber. d. chem. Ges., **11**, 723.

Salzman and Wichelhaus[1] conducted experiments similar to those of Liebermann and Burg, arriving at the same conclusion as regards the filling of the tubes with charcoal and various other substances. Furthermore, they mixed air, acid vapors, etc., with the vapors of the hydrocarbons employed, but obtained no noticeable effect on the resulting tars. They used a brown coal tar, which commenced to boil at 250°, and compared the different results obtained by using eight different fillings for the tubes. The resulting tars varied from a yield of 43 per cent. and a specific gravity 0.9316, obtained by using very large gas coke, up to a yield of 67 per cent., and a specific gravity 0.8869, obtained by the use of platinum asbestos.

Lunge,[2] in 1879, conducted petroleum residues through red-hot tubes, and identified in the product, benzol, toluol, naphthalene, and anthracene.

Williams,[3] in the liquid deposited during the compression of Pintsch gas, found benzol and toluol, ranging in percentage from 25 to 66.

Redwood,[4] by passing the vapors of a petroleum residue through red-hot tubes obtained benzol, naphthalene, and anthracene.

Brochet,[5] in compressed Pintsch gas, identified normal butylene, normal amylene, normal hexylene, and piperylene.

Nikoforoff,[6] by conducting naphtha through red-hot tubes, obtained 12 per cent. benzol and toluol, 0.5 per cent. anthracene, 2.0 per cent. naphthalene, and a tar described as "consisting of hydrocarbons."

Norton and Andrews,[7] by conducting normal hexane through red-hot tubes, obtained ethylene, propylene, crotonylene, amylene, hexylene, and benzol, but no acetylene. From isohexane, at the same temperature, no benzol was formed, but the other products were similar to those from normal hexane. Normal pentane, at a red heat, gave no benzol.

[1] Ber. d. chem. Ges., **11**, 1431.

[2] Industrie des Steinkohlentheers, p. 79.

[3] Chem. News, **49**, 197.

[4] J. Soc. Chem. Ind., 1885, 79.

[5] Compt. rend., **114**, 601.

[6] Eng. Pat. 10,957, 1886.

[7] This JOURNAL, **8**, 1.

Norton and Noyes,[1] by passing ethylene through red-hot tubes, obtained benzol, naphthalene, propylene, butylene, crotonylene, methane, but no acetylene, and from this work they question whether benzol is formed from acetylene, their own theory being that it owes its formation to the olefins.

So far as the actual by-products of oil-gas are concerned, the work of Armstrong and Miller[2] is the most thorough and complete yet done upon the subject. They employed the three different products from the Pintsch gas plants of England—the tar, the gas, and the liquid deposited during the compression of the gas. In the tar they identified benzol, toluol, the xylols, mesitylene, pseudocumene, and naphthalene; in the gas and compressed liquid, crotonylene, valerylene, ethylene, propylene, amylene, hexylene, and heptylene. They assert that in their products there were no true acetylenes, no diphenyl, no olefins higher than heptylene, and no butylene.

Rudnew[3] describes a plant in Russia where benzol is recovered on a commercial scale from oil-gas tar.

Hlawaty[4] passed steam heated to 400° through petroleum, and conducted the vapors produced through red-hot tubes. In a distillate obtained in this way he identified benzol, toluol, xylols, cumol, cymol, styrolene, and anthracene. Acetylene was present in the gas.

Lewes,[5] in the tar obtained by passing the vapors of a Russian oil through red-hot tubes, identified hexane, heptane, nonane, hexylene, heptylene, and benzol.

The most recent, and at the same time probably the most scientific and important work done upon the pyrogenic reactions, was that of Haber and Oechelhäuser[6] upon the decomposition of hexane and of trimethylethylene at different temperatures. The vapors of the hydrocarbon were conducted through a porcelain tube enclosed in a tube of platinum iridium, the latter being heated by the resistance it opposed to the passage of a constant and powerful electric current. The temperature of the retort could thus easily be controlled.

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[1] This JOURNAL, **8**, 362.

[2] J. Chem. Soc., **49**, 74.

[3] Ding. Jour., **239**, 72.

[4] German Pat. 51,553.

[5] J. Soc. Chem. Ind., 1892, 584.

[6] J. of Gas Lighting, 1896.

Between 600° and 700° no decomposition took place, the hydrocarbons first starting to decompose between 780° and 810°. Between 900° and 1,000°, hexane gave the following products: 27.77 per cent. methane; 22.14 per cent. olefins; 1.1 per cent. acetylene; 2.44 per cent. hydrogen; 6.76 to 10.0 per cent. benzol; 3.27 per cent. coke; 29.22 per cent. tar, with a trace of naphthalene. They concluded that, in consideration of their small amounts, acetylene, benzol, coke, and hydrogen could be but side products of these reactions. They attempted to nitrate the tar without removing the unsaturated hydrocarbons and it immediately "carbonized," as it naturally would under these circumstances. Without further investigation they at once concluded that the tar was composed of "condensed olefins." They set 940° as the limit beyond which hexane cannot be heated without considerable decomposition into carbon and hydrogen.

Trimethylethylene, by similar treatment, gave:

1. A similar benzol formation to that of hexane. Since hexane and trimethylethylene have no long chain in common, they concluded that the formation of benzol must be due to polymerization of acetylene.

2. At 935°, more methane than the splitting off of only one CH_3 could account for.

3. Hydrocarbons with closed chains, which, however, were formed with more difficulty than they were from hexane.

Between 668° and 790° they obtained a gas similar to that from hexane, and no separation of carbon and hydrogen could be observed. The tar contained only those olefins which have greater molecular weight than trimethylethylene, while the absence of all higher paraffins they consider especially remarkable. Between 933° and 938°, trimethylethylene gave the following products:

27.72 per cent. methane; 8.10 per cent. ethylene; 1.76 per cent. hydrogen; 4.46 per cent. other gases; 0.30 per cent. acetylene; 5.09 per cent. coke; 8.0–13.4 per cent. benzol; 33.71–39.12 per cent. tar, more methane and benzol being formed at this higher temperature, as was also the case with hexane. They set 950° C. as the limit to which trimethylethylene can be heated before starting to decompose into carbon and hydrogen.

By conducting benzol itself through the retorts they found that it did not start to decompose until the temperature was between 900° and 1,000°, and that the tar thus obtained differed considerably from that given by hexane and trimethylethylene at the same temperature. Hence, they concluded that the compounds in the latter tars must have been condensation-products of benzol, ethylene, etc., rather than decomposition-products of benzol.

We thus see that while considerable work has been done upon the products of the decomposition of paraffin hydrocarbons at high temperatures, the results so far attained, in comparison with those arrived at in the case of coal tar, are meager and in some cases contradictory and unsatisfactory. The following is a summary of all the compounds which have ever been identified in the products arising from such treatment of aliphatic hydrocarbons:

Benzol
Toluol
Xylols
Mesitylene
Pseudocumene
Cumol (?)
Cymol (?)

Naphthalene
Anthracene
Phenanthrene

Ethylene
Propylene
Butylene
Amylene
Hexylene
Heptylene

Acetylene
Crotonylene
Piperylene
Styrolene (?)

Methane
Hydrogen

[We have purposely omitted in the preceding review the results obtained by the simple distillation of petroleum residues, which leads to the formation of "still-wax," believing that they belong rather under the head of the "cracking" of petroleum than to the subject we are discussing. "Cracking" of petroleum seldom or never exceeds 450° C., the only "pyrogenic" reactions taking place in the coke when the latter is heated to redness.]

Considering the fact that the "pyrogenic" reactions have been under investigation for nearly seventy-five years, the progress which has been made is not very great. So many investigators have been content simply to repeat the work of former chemists, and do not know, or at least do not state, the composition of the oil employed, nor make their work quantitative. This is unfortunate, for the question is one which deserves careful consideration, and which offers an almost unlimited field for investigation.

In reading over the literature of the subject one can scarcely fail to be impressed by one peculiar fact, namely, that the products obtained by the action of red heat upon the paraffins *are always the same, no matter what particular hydrocarbons are employed for the experiment.* Now, while coal and petroleum differ in percentage composition they are composed of the same elementary material, and the question suggested itself: Will not petroleum, when treated by destructive distillation, yield a tar exactly similar to coal tar, varying from the latter only in percentage composition? It was in order to investigate this question, and also, if possible, to throw some additional light upon the pyrogenic reactions, that the work described in this paper was undertaken.

In choosing crude heptane and octane as the material to be employed for the experiment, we were influenced by several considerations. In the first place, so far as we are aware, no investigation has ever been made of the decomposition-products of these two hydrocarbons, while those of pentane and of normal and isohexane have received some attention. The crude hydrocarbons were selected in order that the sulphur, nitrogen, and oxygen bodies being still retained, the similarity of the resulting tar to that of coal might be investigated. And we were further influenced in our choice by the fact that the Pintsch plant of the Cleveland Gas Light and Coke Co. was employing exactly the material we had selected, and their treatment of the oil in the retorts was much more complete than we could hope to attain in a laboratory experiment. Through the kindness of this company and of the Recovery Oil Co., which employs their tar, we were able at all times to obtain any material we desired in large quantities. That this was a considerable help may readily be imagined.

The Material Employed.

The heptane and octane employed for the experiment was ordinary 63° naphtha, whose actual gravity at 15° was 0.7310. An assay of this naphtha gave the following figures:

Fraction.	Per cent.
90°–100°	11.0
100°–110°	30.0
110°–120°	27.0
120°–130°	18.0
130°–139°	14.0
	100.0

As hexane boils at 69° and nonane at 150°, there could not have been more than traces of these two hydrocarbons in the heptane and octane, even if present at all. That this naphtha was quite free from impurities was shown by determination of the bromine-absorption and the percentage of sulphur.

In determining the amount of sulphur present, the lamp method of combustion was employed.

1.5860 grams oil required 1.0 cc. of $\frac{1}{16}$-normal NaOH, equivalent to 0.001 gram, or 0.063 per cent. sulphur.

In determining the bromine-absorption a weighed quantity of the oil was placed in a perfectly dry glass-stoppered bottle, dissolved in 15 cc. of carbon tetrachloride, and 10 cc. of a solution of bromine in carbon tetrachloride added. The bottles were then tightly stoppered and left in the dark over night. 25 cc. of a 10 per cent. solution of potassium iodide were then added, and the iodine thus liberated titrated with $\frac{1}{10}$-normal sodium thiosulphate, with the aid of starch paste. Then 15 cc. of a saturated solution of potassium iodate were added. The iodine thus set free by the hydrobromic acid, which had been formed by substitution, was titrated with more thiosulphate.

$\left.\begin{matrix}5.3550\\5.8431\end{matrix}\right\}$ grams oil thus treated required $\left.\begin{matrix}30.8\\25.9\end{matrix}\right\}$ cc. $\frac{1}{10}$-normal $Na_2S_2O_3$ after adding KI, and $\left.\begin{matrix}16.8\\19.2\end{matrix}\right\}$ cc. more after adding the iodate. A blank run at the same time, using the same amount of carbon tetrachloride and bromine solution, required 67.2 cc. $\frac{1}{10}$-normal thiosulphate before adding the iodate, and 8.0 cc. after this addition (this high substitution-figure was due partly to chloroform in the tetrachloride, and, mainly, to acidity of the potassium iodate solution).

Hence, $\left.\begin{array}{l}67.2-30.8=36.4\\ 67.2-25.9=41.3\end{array}\right\}$ cc. $\frac{1}{10}$-normal bromine were used both in adding and in substituting, and $\left.\begin{array}{l}16.8-8.0=8.8\\ 19.2-8.0=11.2\end{array}\right\}$ cc. $\frac{1}{10}$-normal bromine for substituting. And since, for every bromine atom which substitutes, one molecule of hydrobromic acid is liberated, $\left.\begin{array}{l}36.4-(2\times 8.8)=18.8\\ 41.3-(2\times 11.2)=18.9\end{array}\right\}$ cc. $\frac{1}{10}$-normal bromine were used in addition. This gives a result of $\left.\begin{array}{l}2.80\\ 2.61\end{array}\right\}$ per cent. bromine added, and $\left.\begin{array}{l}1.32\\ 1.52\end{array}\right\}$ per cent. bromine substituted.

Treatment of the Heptane and Octane.

The technology of the manufacture of gas from petroleum by the Pintsch process is very simple, and differs only in a few minor details at the various works. The process in use at the Pintsch plant of the Cleveland Gas Light and Coke Co., and by which the naphtha just described was treated, is briefly as follows: The retort consists of a cylinder of cast iron, perhaps 10 feet long and 6 inches in diameter, enclosed in the ordinary clay retort of the gas works, the whole being heated to about 900° C. The iron cylinder consists of three shells or tubes. The oil enters from an exterior pipe in front, drop by drop, into the inner tube, and is at once vaporized. The vapors, after passing through the inner tube, encounter a cap on the end of the next larger tube, which encloses the inner, traverse it in the opposite direction, strike a cap on the front of the largest enclosing tube, and after traversing its length emerge in the rear of the clay retort, which they must pass through in order to make their exit into the hydraulic main. This gives a total distance of about 40 feet which the oil vapors must traverse under the influence of the heat. The arrangement of the hydraulic main, condensers, scrubbers, and purifiers is exactly the same as for coal gas. Very little work is done, however, by any of these save the hydraulic main, which removes the tar, for the impurities found in coal gas are nearly absent from the gas made from oil. After purification the gas is compressed by pumps into welded steel cylinders, perhaps 20 feet long and 5 feet in diameter, where it is kept under a pressure of from 15 to 17 atmospheres.

The Products.

When heptane and octane are treated in the manner just described, they yield as products:

1. A small quantity of a very hard graphitic coke, deposited on the outside of the iron retort.
2. The tar, deposited in the hydraulic main, and equivalent to 25 per cent., by weight, of the original oil.
3. A liquid, designated by the gas men as "hydrocarbon," deposited during the compression of the gas and equivalent to about 10 per cent. by weight of the original oil.
4. The gas itself.

While the actual composition of the tar, as shown by a number of assays, seems to be always the same, the percentage composition varies. This seems to be due to the varying amounts of lower-boiling hydrocarbons which the hot gas carries through the hydraulic main, and which are deposited further on when the gas is compressed. The particular tar which was employed in this research assayed as follows:

The specific gravity at 15° was 0.9369 as opposed to that of the original oil, 0.7310, at the same temperature.

22.5 liters of this tar, when distilled, gave the following products:

		Per cent.
78°–112° (benzol and toluol)	7500 cc.	34.0
112°–200° (xylols, etc.)	3000 cc.	14.0
200°–250° (crude pressed naphthalene)	2600 grams	11.7
200°–340° (oils)	3200 cc.	14.2
Crude pressed anthracene	520 grams	2.3
Solids above anthracene	220 "	1.0
Oils above 340° (containing anthracene)	1000 cc.	4.8
Pitch residue (above 450°)	3260 grams	15.0
		97.0

The bromine-addition of the tar was determined in precisely the same way as that of the original naphtha.

0.2773 gram of the tar was dissolved in 15 cc. carbon tetrachloride and 10 cc. of the bromine solution added. After standing over night, it required 42.8 cc. $\frac{1}{10}$-normal $Na_2S_2O_3$ after adding KI and 14.4 cc. more after adding KIO_3. This gives the bromine-addition 34.48 per cent. and the substitution 18.88 per cent.

The liquid which is deposited during the compression of the gas consists of the lower-boiling hydrocarbons of the tar taken up by the hot gas in its passage through the hydraulic main. The average of a number of assays of this liquid showed about 6 per cent. unsaturated hydrocarbons from 20° to 78°; 80 per cent. of benzol between 78° and 100°; and 10 per cent. toluol and xylols, the loss of 4 per cent. being due to gas dissolved in the liquid. The gas itself will be described further on.

The Aromatic Series.

Nearly every investigator of oil-gas tar has found benzol and toluol, and several have identified the xylols. Armstrong and Miller found mesitylene and pseudocumene, and Hlawaty identified cumol and cymol, but the method of the latter was somewhat irregular. No other hydrocarbon of this series, so far as we know, has ever been identified in the decomposition-products of the paraffins.

For our investigation of the members of this series, 22.5 liters of the tar were distilled from a copper still holding 12 liters, and specially constructed for tar distillation. Up to 270° dry distillation was employed in fractions of 5° each, then the residue distilled with highly superheated steam as long as any distillate would come over. In this way distillates were obtained whose boiling-points ran considerably over 400°. Solid distillates were all cold-pressed and the oils drained off. The separate fractions were then treated in the cold with one per cent. of concentrated sulphuric acid at a time until free from all unsaturated hydrocarbons, washed with water and caustic soda, and dried, It was found that about 6 per cent. concentrated sulphuric acid was required for thorough treatment. All these treated distillates were then repeatedly fractioned, with the aid of Hempel columns, until the right separation was attained.

Benzol.—The fraction boiling from 79°–82° was twice frozen, and the residual oil drained off from the benzol crystals. The benzol thus obtained had a specific gravity of 0.8810 at 10° C., and gave no coloration with strong sulphuric acid, showing its purity.

A quantity of this pure benzol was nitrated, the nitro product washed with water and caustic soda, then distilled with steam. The nitrobenzol thus obtained was a very faintly yellow liquid, which boiled at 205°–206°, and whose specific gravity was 1.203 at 15°, both being correct for pure nitrobenzol. The total quantity of benzol present in this tar was about 18 per cent.

Toluol.—The specific gravity of the 109°–112° fraction was 0.8603 at 15° C. It was nitrated and the nitro products washed and distilled with steam. This distillate was dried and fractioned. The orthonitrotoluol boiled at 223°–225°, was faintly yellow, and its specific gravity was 1.157 at 15°, showing its purity. The percentage of toluol in the tar was about 12.

Xylols.—A cold mixture of sulphuric and nitric acids, shown by Jacobsen to be capable of distinguishing a very minute quantity of orthoxylol in a mixture of the three, immediately gave in the 135°–145° fraction an oily layer between the acids and the hydrocarbons, showing the presence of orthoxylol.

For the detection of meta- and paraxylols, the following method, which we have not found described elsewhere, gave fair results: About 50 cc. of the mixed xylols were gently heated for some time with a mixture of chromic and sulphuric acids in a flask with return condenser. By this treatment orthoxylol is completely burned to carbon dioxide and water, metaxylol gives isophthalic acid, paraxylol gives terephthalic acid. When oxidation was completed the mixture was poured into cold water, and the precipitated acids filtered and washed with cold water, then dissolved in caustic soda and reprecipitated with hydrochloric acid, this being repeated until the acids were obtained pure. They were then dissolved in ammonia and the solution just neutralized with hydrochloric acid. Barium chloride was then added in the slightest possible excess, precipitating all the terephthalic acid as barium terephthalate. This was filtered and hydrochloric acid added, in excess, to the filtrate precipitating isophthalic acid.

While attempting to secure further proof of the presence of meta- and paraxylols by forming the sulphonic acids, we, unfortunately, lost the rest of this fraction, and, having no more of this distillate, could make no further tests. But we think there can be no doubt of the presence of the three xylols. Their percentage in the tar was about 5.

The members of the aromatic series boiling above 150° are still under investigation, and will receive further attention. We may state, however, that we have fractions of highly refractive liquids, boiling all the way from 150° to above 300°, and we hope soon to be able to determine the composiof these distillates, which are equivalent to 20 per cent. of the tar.

Compounds with Condensed Benzol Nuclei.

Naphthalene, anthracene, and phenanthrene were the only members of this series which had ever been identified in such tars.

Naphthalene.—The distillate between 200° and 250° was cooled and the solids pressed free of oils. This crude pressed naphthalene was quite pure, its melting-point being 78°. When sublimed it gave the proper melting-point, 79°. The percentage of naphthalene in this tar was 11.8.

In fractioning the oils between 150° and 300°, some naphthalene was contained in all the distillates from 200° to 260°. As diphenyl boils at 254°, it was thought that it might be contained in the solids of the 250°–255°, and 255°-260° fractions. But the latter, when drained and pressed, melted at 78°, and, when recrystallized from hot alcohol, at 79°, showing it to be naphthalene. Diphenyl melts at 71°, and its presence here could hardly have failed to change the melting-point of the naphthalene. While diphenyl has often been sought for in the oil-gas tars it has never been found. It seems rather curious that it should not occur along with the other condensed-ring hydrocarbons.

Anthracene.—The solid which came over with steam after the oils above naphthalene had distilled was a yellow oily mass. The oils were removed by cold-pressing, and the crude anthracene thus obtained was a butter-yellow.

50 grams were dissolved in glacial acetic acid and oxidized with 90 grams chromic acid, the excess of acetic acid distilled off, and the residue poured into water. The brown precipitate was filtered and washed with water, then warmed with a solution of acid sodium sulphite to remove phenanthraquinone, filtered, and washed with water. The residual anthraquinone was dried and sublimed, giving the characteristic golden needles of anthraquinone, melting at 285°. The amount of anthracene present in the tar was about 3 per cent.

Phenanthrene.—Dilute sulphuric acid, when added in slight excess to the solution in acid sodium sulphite, gave a yellow precipitate. This was filtered, washed, and dried, and then crystallized from hot benzol. The phenanthraquinone thus obtained had a constant and correct melting-point, 198°. There was about 0.4 per cent. phenanthrene in the tar.

Chrysene.—The steam distillate above anthracene was an oily, reddish-yellow solid. It was pressed and then washed with petroleum ether to remove all oil. The solid thus obtained was a yellow meal. This solid was repeatedly extracted with carbon disulphide and filtered. The residue was greenish-white, very sparingly soluble in hot alcohol, and somewhat readily soluble in hot benzol, the latter solution having the beautiful violet fluorescence characteristic of chrysene. It was repeatedly crystallized from hot benzol, separating in small greenish-white leaflets. The melting-point remained constant at 250°, which is correct for chrysene. To still further identify the chrysene, it was dried, and a portion oxidized to the quinone by suspending it in glacial acetic acid, adding chromic acid slowly, boiling after each addition, and filtering while boiling hot. The filtrate, when diluted with water, gave an orange-red precipitate, which was filtered and washed. A single particle of this quinone with concentrated sulphuric acid, gave the deep blue color so characteristic of chrysenequinone. There was about 0.4 per cent. chrysene in the tar.

Fluoranthene?—The carbon disulphide solution obtained upon extracting the chrysene was distilled, and the residue extracted again with a little carbon disulphide. It was found that more chrysene was obtained by this treatment, which was continued until all the chrysene had been removed. A small portion of the residue, which was yellow, when dissolved in warm sulphuric acid, gave the deep blue fluorescence said to characterize fluoranthene, but there was not enough of it to enable us to further identify it.

Aliphatic Hydrocarbons.

Armstrong and Miller,[1] in forming the sulphonic acids of the benzol fraction of Pintsch-gas tar found that not all of the hydrocarbon would dissolve in fuming sulphuric acid, and this residue, after distillation in steam over a little alkali, they describe as a clear, brilliant oil with the "sweet odor of a true paraffin." They did not have enough of this oil to enable them to identify it, but concluded that it was composed both of paraffins and "pseudolefins," or the so-called naphthenes. It is probably upon the strength of this surmise that Lunge[2] makes the incorrect statement that Armstrong and Miller found the naphthenes in Pintsch-gas tar.

In the course of our work upon the aromatic series in the tar we found just such an oil as Armstrong and Miller describe, and went to considerable pains to determine its nature. It was noticed that upon nitrating benzol and then distilling in steam, the first distillate was a brilliant oil of low specific gravity, amounting to not more than 4 per cent. of the hydrocarbon taken, and insoluble in fuming sulphuric acid. Two liters of this distillate were obtained at the works of the Recovery Oil Co., and the hydrocarbons separated by distillation from the nitrobenzol contained. The distillate thus obtained had a peculiar sour smell and the specific gravity 0.7306 at 15° C. It was treated with fuming sulphuric acid in the cold until no further action took place, then washed with caustic soda and water. By this treatment only about 3 per cent. of the oil was removed, the specific gravity remaining practically the same—0.7280 at 15°—but the sourness was removed, leaving a very sweet and pleasant smell.

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[1] *Loc. cit.*

[2] Industrie des Steinkohlentheers.

Upon nitrating 1100 cc. of toluol and then distilling in steam, 90 cc. or 8.2 per cent. of a similar inert oil was obtained, whose gravity was 0.7316 at 15°. This was added to that obtained from the benzol, and the whole of this oil, amounting to about a liter, very carefully fractioned over sodium, finally a number of times at 1° intervals. It all distilled between 90° and 130°, and collected chiefly at 98°–99° and 118°–120°.

Two vapor density determinations of the 98°–99° fraction gave 49.2 and 50.8. Heptane, boiling at 98°–99°, has the vapor density of 50, hexahydrotoluol, boiling at the same point, has the vapor density of 49. The specific gravity of heptane is given by Thorpe as 0.6885 at 15°, while that of hexahydrotoluol is 0.7723 at 0°. The observed specific gravity of our distillate was 0.7219 at 15°, which, while higher than that assigned to heptane, yet agrees closely with those observed for the same distillates of American petroleum. In order to determine whether, as is thought by many to be the case in petroleum distillates, this heptane fraction owed its higher specific gravity to the presence of a naphthene, portions were boiled with a mixture of sulphuric and nitric acids for definite periods, and the specific gravities of the original and residual oils compared. But in no single instance, even after two-thirds of the original oil had been destroyed, was the least change in the specific gravity noted. Carbon and hydrogen determinations in this fraction gave the following results :

0.1540 gram oil gave 0.4727 gram CO_2, and 0.2230 gram H_2O.

	Calculated.	Found.
$\begin{cases} C_7 \\ H_{16} \end{cases}$	84.00 16.00	83.71 16.08
$\begin{cases} C_7 \\ H_{14} \end{cases}$	85.71 14.29	....

All these results tend to show that the hydrocarbon was normal heptane and that no naphthene was present.

The specific gravity of the octane boiling at 119°, is

0.7188 at 0°, that of hexahydroisoxylol, boiling at 118°, is 0.7814 at 0°. The observed specific gravity of our distillate, 118°–120°, was 0.7292 at 15°. The action of sulphuric and nitric acids caused no noticeable change in specific gravity even after 55 per cent. had been destroyed, and a combustion gave the following results :

0.1864 gram oil gave 0.5781 gram CO_2, and 0.2615 gram H_2O.

	Calculated.	Found.
$\left\{\begin{array}{l} C_8 \\ H_{18} \end{array}\right.$	84.21 15.79	84.54 15.58
$\left\{\begin{array}{l} C_8 \\ H_{16} \end{array}\right.$	85.71 14.29	....

Hence, this fraction was octane and no naphthenes could have been present.

While treating these hydrocarbons with sulphuric and nitric acids, as before described, some interesting facts were noted. Thus, heptane, after being boiled for an hour with the acid mixture, gave in the wash water of the residual oil the characteristic odor of butyric acid, while upon another occasion valerianic acid seemed to be formed. While numerous chemists have noticed these reactions during their investigation of the composition of petroleum,[1] it is still a question as to just what reactions take place and what products are obtained by the action of these acids upon the paraffins.

In treating the octane fraction in this way, 100 cc. of the oil were gently boiled with 100 cc. sulphuric and 100 cc. nitric acids for fourteen hours. The liquid, on cooling, separated into three distinct layers. The lower layer of acids was drawn off and afterwards thrown away by mistake. The upper two layers were shaken with water, causing the separation of an oily, nitro-like body, whose gravity was nearly that of water.

The residual hydrocarbon was yellow and was extracted with strong sulphuric acid until colorless. It had been found in previous experiments that while caustic soda acted but slowly in extracting these compounds, sulphuric acid worked readily, taking a deep-red color from the extracted body. The sulphuric acid extract was poured into water, cooled, extracted with ether, and the ether distilled off. The residue was a yellow, fatty-smelling compound. 5.44 grams of this were dissolved in alcohol and titrated with 37.8 cc. of normal alcoholic potassium hydroxide. Calculating it as an acid and as monobasic, this gives 143.9 as the molecular weight. The molecular weight of octoic acid is 144. The copper salt was formed and crystallized well, but no further work was done upon it.

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[1] Beilstein and Kurbatow: Ber. d. chem. Ges., **13**. 2028; Mabery: Proc. Am. Acad., **32**, 6.

The heavy nitro-like body before mentioned was tested with potassium hydroxide, potassium nitrite, and sulphuric acid for a nitroparaffin. But the solution in potassium hydroxide gave such an intense red color in itself that the test proved nothing. By dissolving a weighed quantity in alcohol, adding excess of normal potassium hydroxide, and titrating back with normal hydrochloric acid, it was found to be a neutral compound.

Konowalow[1] obtained nitrohexane by heating normal hexane to 135° with nitric acid af 1.075 specific gravity. Beilstein and Kurbatow[2] made nitroheptane by boiling the 95°–100° fraction of American petroleum with nitric acid of specific gravity 1.38. It is possible that the compounds we obtained from octane by this treatment with sulphuric and nitric acids were nitrooctane and octoic acid. While the whole subject is very interesting, and one which deserves more attention, it was outside the scope of our subject and was not further investigated.[3]

The presence of aliphatic hydrocarbons having thus been proved, the question arose: Did merely the unchanged heptane and octane occur in the products, or were there lower paraffins also, formed by the decomposition of the two former? As we have seen, nearly every theory of the pyrogenic reaction is based upon the assumption that the higher paraffins split up into lower molecules of the same series. Now, if heptane and octane are able to pass through these red-hot retorts unchanged, as we found to be partly the case, any lower paraffins which are still more stable would certainly be able to do the same. Hence, if lower paraffins are formed, they would necessarily be present to some extent among the products.

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[1] Ber. d. chem. Ges., **25**, [2] 198.

[2] Ber. d. chem. Ges., **13**, 2029.

[3] The action of these reagents upon the paraffins is now being carefully investigated by the author.

The liquid which was noticed as being deposited during the compression of the gas, commences to boil at a very low temperature, and upon being warmed, gives off a considerable amount of gaseous hydrocarbons. The gas given off upon starting a still holding 2,000 gallons of this liquid at the works of the Recovery Oil Co. was passed into two pounds of bromine, kept cool and in the dark. But no gas passed through the bromine even after a rapid stream had been running for several hours. Hence, nothing but unsaturated hydrocarbons could have been present in this lower-boiling portion of the liquid. And upon testing that portion of the liquid itself which boils between 20° and 78°, nothing was found which was insoluble in fuming sulphuric acid, nor was there anything in the distillate above 130° insoluble in the acid. Hence no other paraffins than the original heptane and octane were present in the tar and compressed liquid. The discussion of their presence in the gas itself will be found further on.

Naphthenes.

So far as we could find, no work whatever had ever been done upon the occurrence of naphthenes in oil-gas tar. Although we had proved their absence from that inert hydrocarbon which could not be nitrated or dissolved in fuming sulphuric acid, and which Armstrong and Miller assumed to contain naphthenes, this was not conclusive proof of their absence from the products, for, according to Beilstein, a mixture of sulphuric and nitric acids, when heated, gives with the naphthenes the nitro compounds of the corresponding aromatic hydrocarbons. And where this nitration is carried on with large quantities of the hydrocarbons, and in a commercial way, as is the case at the works of the Recovery Oil Co., the mixture is almost sure to become heated. Then, too, it seems to be a disputed question as to whether or not the naphthenes are soluble in fuming sulphuric acid in the cold, and it was thought best to determine their presence in or absence from the original tar.

For hexahydrobenzol boiling at 69°, 2 liters of a distillate 68°–70° from the compressed "hydrocarbon" were treated in the cold with an excess of concentrated sulphuric acid until all unsaturated hydrocarbons were removed. The residue, of which there was about one liter, was washed with water and caustic soda, dried, and fractioned. Only 50 cc. distilled below 78°, the rest being benzol. The lower distillate was again treated with sulphuric acid, washed, and dried. Repeated fractioning showed this to be benzol, and nothing would distil below 77°. For hexahydrotoluol, boiling-point 97°, and hexahydroisoxylol, boiling-point 118°, 15 liters of the distillate which comes off the tar with tight steam coil, and which are equivalent to about 60 liters of tar, were employed. This was first distilled at 10° limits, then thoroughly treated with sulphuric acid, washed, and dried. The treated distillates were then repeatedly fractioned, first at 5° then at 3° intervals, finally a number of times at 2° limits. A final fractioning showed the following results between 94° and 100°.

	Volume. cc.	Per cent. in tar.	Specific gravity at 20° C.
94°–96°	100	0.17	0.8620
96°–98°	90	0.15	0.8606
98°–100°	70	0.12	0.8588

The specific gravity of hexahydrotoluol is 0.7723 at 0°, and the presence of any appreciable amount would have increased the volume and lowered the specific gravity of the 96°–98° fraction. But both the volume and the specific gravity show only the normal decrease from the benzol to the toluol fractions.

Similarly, no bunching or decrease in specific gravity could be observed in the 118°–120° fraction, where hexahydroisoxylol should occur. Considering the large amount of tar employed and the careful fractioning, it seems certain that no naphthenes were present in the products.

Unsaturated Hydrocarbons.

As shown by the bromine absorption of the tar—33.48 per cent.—unsaturated hydrocarbons are present in considerable amount. These unsaturated hydrocarbons of the gas, the tar, and the compressed liquid will be investigated soon.

The absence of true acetylenes in the tar and compressed liquid has been established, however, by passing the gas from 2,000 gallons of the compressed liquid through ammoniacal cuprous solution. After running at a rapid rate for several hours the gas failed to give any indication of acetylenes, and the liquid itself, when tested with the solution, also gave a negative result.

Oxygen, Nitrogen, and Sulphur Compounds.

So far as we are aware, no attempt had ever been made even to determine the presence of sulphur, nitrogen, or oxygen in oil-gas tars. The question of the formation of compounds of these three classes seemed to us an important one, for if it could be proved that typical members of these groups were present, the similarity of this tar to coal tar would be established.

Phenols.—The phenols were taken as the type of the oxygen compounds occurring in coal tar, and were tested for in the following manner: The untreated distillates of the 22.5 liters of tar between 145° and 210° were thoroughly extracted with caustic soda. This solution was then made slightly acid with hydrochloric acid, and the unmistakable odor of carbolic acid at once became apparent. This slightly acid solution was then extracted with ether, and the ether distilled off from the extract, leaving 1.2716 grams or 0.05 per cent. phenols. This is equivalent to about a pound per ton of tar.

Ferric chloride in neutral solution of this residue gave a violet coloration, and bromine water caused a yellow precipitate of tribromphenol. Hence, carbolic acid was present, and although there was not enough material to test for the higher homologues, it is probable that they also occur in the tar.

Ammonia.—Ammonia was taken as the type of the nitrogen compounds of coal tar. In order to test for ammonia, 2 liters of the water which flows through the scrubbers of the Pintsch-gas works in a small but continuous stream were obtained at the exit. This water showed a faint alkalinity. 500 cc., when titrated, required 0.3 cc. $\frac{1}{16}$-normal hydrochloric acid, equivalent to 0.00006 per cent. free ammonia, or thirty times the amount contained in the lake water itself. The 2 liters of water were made slightly acid with sulphuric acid and evaporated to a small volume. A slight excess of caustic soda was then added, and two-thirds distilled off into 30 cc. of the standard hydrochloric acid. 1.3 cc. of this $\frac{1}{16}$-normal acid were required, which gave 0.000068 per cent. total ammonia. Hence the ammonia was practically all present in the free state.

The percentage of nitrogen in the tar was determined by the Kjeldahl method.

4.2739 grams tar required 2.5 cc. $\frac{1}{16}$-normal hydrochloric acid, equivalent to 0.053 per cent. ammonia, or 0.042 per cent. nitrogen. A qualitative test of the tar for ammonia failed to show the least trace. Hence there are probably nitrogen bases formed in addition to the ammonia.

Sulphur Compounds.—In determining the amount of sulphur present in the tar, it was found that a sufficiently high temperature for complete combustion could not be attained in a combustion furnace without the use of oxygen, and that the lamp method gave good results.

0.9374 gram tar by the latter method gave 0.0005 gram sulphur or 0.053 per cent.

Thiophene was tested for in all the distillates of crude benzol with isatine and sulphuric acid, but could not be detected. In the water which is drawn off with the tar from the hydraulic main, lead acetate failed to give any blackening, but in another portion the addition of a little caustic soda and sodium nitroferricyanide gave the characteristic purple color showing the presence of hydrogen sulphide.

The Gas.

In determining the composition of the gas formed by the heptane and octane, the chief object in view was to investigate the presence of hydrogen, acetylene, methane, and the higher paraffins. The formation of hydrogen and acetylene by the pyrogenic reactions is still a disputed question. J. B. Lewes,[1] in the gas obtained by passing Russian petroleum through tubes heated to between 900° and 1000°, found from 12 to 22 per cent. hydrogen, and from 0.38 to 0.46 per cent. acetylene. Pryce and Hunt,[2] by passing Russian oil through retorts whose temperatures varied from 600° to 1060°, found hydrogen *always* present in the gas, ranging in percentage from 16 to 57, along with from 23 to 51 per cent. methane. Haber and Oechelhäuser,[3] however, assert that from hexane they obtained no hydrogen until the temperature reached 900°, and between 900° and 1000° only 2.44 per cent. along with 1.10 per cent. acetylene and 27.77 per cent. methane, while Norton and Andrews,[4] from normal and isohexane, could obtain no acetylene. While there thus seem to be conflicting opinions about the formation of hydrogen and acetylene from paraffins under the influence of heat, methane is always found in considerable quantity and *never associated with higher homologues*.

A large gasometer full of the gas made from the heptane and octane was obtained directly from the compression tanks of the Pintsch plant, and its constituents determined in the following way: Carbon dioxide by potassium hydroxide solution; oxygen by pyrogallol; acetylene by ammoniacal cuprous chloride; the other luminants by fuming sulphuric acid; hydrogen by absorption in palladium sponge; and methane by exploding the residue. Carbon monoxide and nitrogen were determined independently; carbon monoxide by first removing all luminants, then absorbing in ammoniacal chloride; nitrogen by exploding this residue.

Considering the high pressure upon the gas, the aromatic hydrocarbons could hardly have been present, or at least only to a very small extent. In determining methane, a measured volume of the gas residue was mixed with a measured volume of oxygen and exploded in a pipette over strong sulphuric acid. The contraction here was due to the water vapors absorbed by the acid, and by passing into potassium hydroxide the amount of carbon dioxide was determined. In every case the volume of oxygen actually used for the explosion was just twice that of the gas taken, less the nitrogen it contained; the volume of carbon dioxide formed was equal to that of the gas less the nitrogen; and the volume of water vapor twice as great, thus showing the residual hydrocarbon to have been all methane, according to the reaction:

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[1] J. Soc. Chem. Ind., 1892, 584.

[2] Gas World, **18**, 511.

[3] *Loc. cit.*

[4] *Loc. cit.*

$$\begin{array}{lccccccc} & \mathrm{CH_4} & + & 2\mathrm{O_2} & = & \mathrm{CO_2} & + & 2\mathrm{H_2O}, \\ \text{Volumes} & 1 & & 2 & & 1 & & 2 \end{array}$$

while from the nature of the reactions of ethane and higher homologues,

$$\begin{array}{lccccccc} & \mathrm{C_2H_6} & + & 3\tfrac{1}{2}\mathrm{O_2} & = & 2\mathrm{CO_2} & + & 3\mathrm{H_2O}, \\ \text{Volumes} & 1 & & 3\tfrac{1}{2} & & 2 & & 3 \\ & \mathrm{C_3H_8} & + & 5\mathrm{O_2} & = & 3\mathrm{CO_2} & + & 4\mathrm{H_2O}, \text{ etc.}, \\ & 1 & & 5 & & 3 & & 4 \end{array}$$

we see that these higher paraffins could not have been present.

The percentage composition of the gas, taken from the average of several determinations, was as follows:

Nitrogen[1]	11.8
Acetylene[2] (and ethylene?)	11.3
Other luminants	15.5
Hydrogen	18.4
Methane	42.9
	99.9

Summary.

It has been observed at the Pintsch plant that 16 gallons of this naphtha always give about the same quantity of each product—3 gallons of tar, 1.5 gallons of "hydrocarbon," and 1,000 cubic feet of gas. Calculating from these figures and from the specific gravities and percentage composition of these several products, we find that crude heptane and octane, containing small quantities of sulphur, nitrogen, and oxygen compounds, gave, when decomposed at about 900°, solid, liquid, and gaseous products of the following nature and amounts :

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[1] The nitrogen was doubtless due to air introduced by the pumps during the compression of the gas, the corresponding oxygen having been absorbed by the unsaturated hydrocarbons deposited at the same time, which were found to take up oxygen readily.

[2] Hempel has shown that ammoniacal cuprous chloride slowly absorbs ethylene. Hence the figure obtained for acetylenes probably represents some ethylene also, for considerable difficulty was experienced in obtaining satisfactory duplicates of this determination, which was made as rapidly as possible. A large amount of acetylene was present, however, for, whenever the gas was passed into the ammoniacal cuprous chloride, it gave a heavy red deposit of cuproacetylene.

	Percentage by weight.
Olefins	26.0
Methane	25.1
Benzol	12.5
Acetylene (and ethylene?)	12.1
Toluol	3.0
Xylols, etc. (120°–200°)	3.0
Aromatic hydrocarbons (200°–300°)	4.5
" " (above 300°)	2.3
Naphthalene	3.6
Anthracene	1.3
Phenanthrene	0.1
Chrysene	0.1
Fluoranthene(?)	about 0.01
Pitch	4.1
Hydrogen	1.4
Phenols	0.01
Ammonia and nitrogen bases	small amounts
Hydrogen sulphide	" "
Coke	" "
Naphthenes	absent
Thiophene	"
Diphenyl	"
Higher acetylenes	"
Paraffins, other than methane	"
Total	99.1

Upon consulting this table one notices that the olefins, methane, acetylene, and the aromatic hydrocarbons seem to be the chief products of the reaction, for, taken together, they constitute 88.5 per cent. of the total product. The method of their formation, however, is another question. Whether the higher aromatic hydrocarbons are formed directly by the reaction or are only secondary products owing their formation to the decomposition of benzol; whether acetylene is a primary product or is formed by decomposition of the olefins; whether benzol owes its formation to the polymerization of acetylene; of these and many other problems the table gives no solution. We see, moreover, that more methane is formed than the splitting off of only one methyl group from heptane or octane can account for, more hydrogen than the liberation of only one molecule from either hydrocarbon can explain.

We see also that the products yielded by the naphtha are almost exactly identical with those obtained from coal by similar treatment. This does not, however, imply any great similarity between the constitution of coal and of petroleum, for if we review the work which has been done upon the products of the pyrogenic reactions, we are confronted by some peculiar facts. We see that practically the same products were obtained by Letny from petroleum hydrocarbons, none of which could have been below pentadecane, as by Haber from hexane and from amylene; by Haber from hexane and from amylene, as by Berthelot from acetylene; by Norton and Noyes from ethylene, as by Haber from hexane; by Berthelot[1] from toluol, from xylol, and from cumol, as from acetylene; and, finally, by the author from crude heptane and octane, as by Berthelot from the aromatic hydrocarbons, and by countless investigators from coal.

Hence it would seem, *that all hydrocarbons, under similar conditions of temperature, yield the same products.* What theory so far advanced explains all the facts? Schulze's explanation of the formation of coal-tar hydrocarbons from the phenols cannot be correct, for the same hydrocarbons are formed from compounds which contain no oxygen. If Berthelot, Haber, and all the others who explain such reactions by assuming that the paraffins first split up into lower molecules are correct, why are not these lower paraffins found among the products, and why do hydrocarbons which do not belong to the paraffin group—ethylene and xylol, for example—yield the same products as the paraffins? What theory so far advanced explains the formation of *methane*, and of *that alone*, of the aliphatic hydrocarbons, and its presence in such great quantity? What hypothesis makes clear why substances apparently so widely different as coal and petroleum, olefins and paraffins, acetylenes and the aromatic hydrocarbons, should

[1] Bull. Soc. Chim. [1], 7, 217.

all yield the same products, or can tell us just why those products and no others should be formed in each case?

To the author it seems that these problems have not yet been solved—that the "pyrogenic" reactions, simple or complex as they may be, have never yet been explained, and it is to be hoped that further investigation of this important subject may assist in giving a clearer conception of these peculiar reactions.

In conclusion, the author desires to express his sincere thanks to Dr. A. W. Burwell, not only for the use of his private laboratory, which he so generously placed at my disposal, but also for his constant and valuable aid during the course of the investigation.

Contributions from the Chemical Laboratory of Cornell University.

ANETHOL AND ITS ISOMERS.

BY W. R. ORNDORFF, G. L. TERRASSE, AND D. A. MORTON.

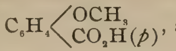
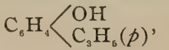
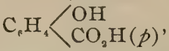
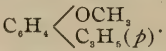
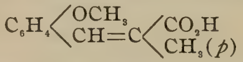
Few substances among the compounds of carbon are known in more isomeric modifications than anethol, the chief constituent of the well known oil of anise. No less than nine of these isomers have already been made and described. The names of these are as follows: (1) methyl ether of orthopropenylphenol, (2) methyl ether of metapropenylphenol, (3) methyl ether of chavicol, (4) estragol, (5) fluid metanethol, (6) anisoïn, (7) solid metanethol, (8) isoanethol, and (9) photoanethol.

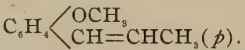
Comparatively little is known concerning the relation of these substances to each other or to anethol, and in most cases not even the molecular weight has been determined. We have therefore undertaken the study of some of these substances in the hope that we might be able to throw some light on this complicated chapter of the science. Before giving the experimental work, it will be well briefly to review the literature of the subject so that the present state of our knowledge may be clear.

Anethol.

Anethol itself was first carefully studied by Cahours,[1] who

[1] Ann. chim. phys. [3], **2**, 274; **14**, 489.

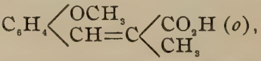
showed that it had the formula $C_{10}H_{12}O$, and gave anisic acid,  $C_6H_4\Big\langle\begin{array}{l}OCH_3\\CO_2H(p)\end{array}$, and acetic acid on oxidation. Ladenburg and Leverkus[1] then found that with hydriodic acid anethol gave methyl iodide, while on fusion with potassium hydroxide paraanol,  $C_6H_4\Big\langle\begin{array}{l}OH\\C_3H_5(p)\end{array}$, together with some paroxybenzoic acid,  $C_6H_4\Big\langle\begin{array}{l}OH\\CO_2H(p)\end{array}$, resulted. With bromine it very readily formed a dibrom addition-product, $C_{10}H_{12}Br_2O$, and all attempts to replace the oxygen atom in anethol by two atoms of chlorine, by treatment with phosphorus pentachloride, failed. This work with that of Cahours shows that the formula of anethol is  $C_6H_4\Big\langle\begin{array}{l}OCH_3\\C_3H_5(p)\end{array}$. The structure of the C_3H_5 group was then determined by Perkin,[2] who made anethol synthetically by heating paramethoxyphenylcrotonic acid,  $C_6H_4\Big\langle\begin{array}{l}OCH_3\\CH=C\Big\langle\begin{array}{l}CO_2H\\CH_3(p)\end{array}\end{array}$, to its boiling-point, and also by treating the hydrobromic acid addition-product of this acid with a solution of sodium carbonate. Anethol must hence have the following structural formula :



$$C_6H_4\Big\langle\begin{array}{l}OCH_3\\CH=CHCH_3(p).\end{array}$$

Anethol is described as an oil with a pleasant odor of anise, crystallizing in plates, which melt at 21.1° C., and boiling at 233° to 233°.5 C. at 751.1 mm. Specific gravity 0.98556 at 21°.6 C. as compared with water at 4° C.

Methyl Ether of Orthopropenylphenol.

This isomer of anethol was made by Perkin[3] by treating the hydriodic acid addition-product of either the α- or the β-orthomethoxyphenylcrotonic acid,  $C_6H_4\Big\langle\begin{array}{l}OCH_3\\CH=C\Big\langle\begin{array}{l}CO_2H\ (o)\\CH_3\end{array}\end{array}$, with a solution of sodium carbonate. It is a liquid boiling at 222°–223° C., and having a specific gravity of 0.989, at 30° C.

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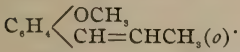
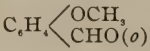
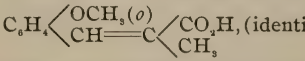
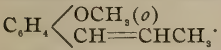
[1] Ann. Chem. (Liebig), Supl. Bd., **8**, 88, and **141**, 260.

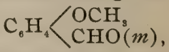
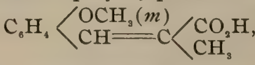
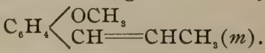
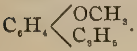
[2] J. Chem. Soc., **31**, 412 ; **33**, 211 ; **39**, 445. See also in this connection Moureu and Chauvet, Bull. Soc. Chim. (Paris), [3], **17**, 411.

[3] J. Chem. Soc., **33**, 213 : **39**, 434.

From its method of formation it must have the formula  $C_6H_4\left\langle\begin{array}{l}OCH_3\\CH{=}CHCH_3(o)\end{array}\right.$.

This same ether was made by C. Mouren[1] by heating the methyl ether of salicylic aldehyde,  $C_6H_4\left\langle\begin{array}{l}OCH_3\\CHO(o)\end{array}\right.$, with propionic anhydride and fused sodium propionate. Methyl-*o*-propiocumaric acid,  $C_6H_4\left\langle\begin{array}{l}OCH_3(o)\\CH{=}C\left\langle\begin{array}{l}CO_2H\\CH_3\end{array}\right.\end{array}\right.$, (identical with Perkin's α-methyl-*o*-oxyphenylcrotonic acid), is first formed, and this by the loss of carbon dioxide forms the compound  $C_6H_4\left\langle\begin{array}{l}OCH_3(o)\\CH{=}CHCH_3\end{array}\right.$. This product is described by Mouren as a liquid boiling at 220°–223° C. at normal pressure, having an odor resembling veratrol, specific gravity of 1.0075 at 0° C., and which does not solidify at —23° C. It readily absorbs one molecule of bromine. From this description of its properties and the mode of formation, there can be no doubt of the identity of the two products. Mouren calls this product orthoanethol.

Methyl Ether of Metapropenylphenol.

This product was also made by C. Mouren, using the methyl ether of methoxybenzoic aldehyde,  $C_6H_4\left\langle\begin{array}{l}OCH_3\\CHO(m)\end{array}\right.$, and heating with propionic anhydride and fused sodium propionate. A similar reaction takes place here as in the case of the formation of the ortho ether of propenylphenol. Methyl-(*m*)-propiocumaric acid,  $C_6H_4\left\langle\begin{array}{l}OCH_3(m)\\CH{=}C\left\langle\begin{array}{l}CO_2H\\CH_3\end{array}\right.\end{array}\right.$, is first formed, and this by the loss of carbon dioxide, gives the methyl ether of metapropenylphenol,  $C_6H_4\left\langle\begin{array}{l}OCH_3\\CH{=}CHCH_3(m)\end{array}\right.$. This method of formation fixes the structure of the compound to which Mouren gives the name metaanethol. It is a liquid distilling at 226°–229° C. (uncorr.) at ordinary pressures, and having an odor recalling that of elenic resin. Its specific gravity at 0° is given as 1.0013. It remains liquid when cooled to 23° C., and in chloroform solution at 0° absorbs readily one molecule of bromine. Neither the ortho nor the metaanethol has as yet been found in nature. Mouren made no determinations of the molecular weight of these ethers of propenylphenol, but it is very probable from the mode of formation that they are correctly represented by the formula  $C_6H_4\left\langle\begin{array}{l}OCH_3\\C_3H_5\end{array}\right.$.

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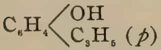
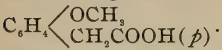
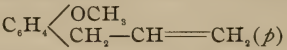
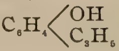
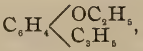
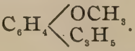
[1] Compt. rend., **123**, 157; Bull. Soc. Chim. (Paris), [3], **15**, 1021.

Methyl Ether of Chavicol.

This substance was made by Eykman[1] in 1888 from chavicol,  $C_6H_4\left\langle\begin{array}{l}OH\\C_3H_5\ (p)\end{array}\right.$, which he obtained from Bette leaves. It closely resembles anethol in boiling-point (226° C.), and in other physical properties, though it does not solidify even at — 25° C. It has the odor and taste of anise, but weaker than in anethol. It is converted into anethol on boiling with a solution of alcoholic caustic potash, and on oxidation it gives anisic and paramethoxyphenylacetic acid,  $C_6H_4\left\langle\begin{array}{l}OCH_3\\CH_2COOH(p)\end{array}\right.$. From these facts Eykman regards methylchavicol as containing the normal allyl grouping and having the formula,  $C_6H_4\left\langle\begin{array}{l}OCH_3\\CH_2{-}CH{=\!=}CH_2(p)\end{array}\right.$. He finds a further confirmation of this formula in a comparison of the optical constants of methyl chavicol with those of anethol and by a comparison of these constants with those of other compounds known to contain an allyl and a propenyl grouping. Eykman determined the molecular weights of chavicol and of ethylchavicol by the vapor-density method, as well as by the freezing-point method, and found that they agreed with the formulas  $C_6H_4\left\langle\begin{array}{l}OH\\C_3H_6\end{array}\right.$ and  $C_6H_4\left\langle\begin{array}{l}OC_2H_5\\C_3H_6\end{array}\right.$, respectively, so that it is highly probable that the methyl ether of chavicol has the formula  $C_6H_4\left\langle\begin{array}{l}OCH_3\\C_3H_5\end{array}\right.$.

Estragol.

Estragol was first made by Grimaux[2] in 1894 from estragon oil by repeated fractional distillation. He gives the boiling-point 215°–216° C. (corr.), and as this differs from the boiling-point of anethol by about 16°—the usual difference in boiling-point of compounds known to contain the allyl and propenyl grouping, (eugenol and isoeugenol, safrol and isosafrol, apiol and isoapiol),—he is inclined to regard estragol as containing the normal allyl grouping, $C_6H_4\left\langle\begin{matrix}OCH_3\\CH_2CH{=}CH_2\end{matrix}\right.$. Like methyl chavicol, it is converted into anethol on heating with an alcoholic solution of potassium hydroxide, and does not solidify at a temperature of — 43° C. Methyl chavicol, Grimaux thinks, may be a stereoisomer of anethol, though he adduces no reason for this view, nor does he state whether he regards it as a cis or a trans compound. He did not determine the molecular weight of estragol, so that we do not know whether it is a metamer or a polymer of anethol. In 1892, some two years before this work of Grimaux on estragol, Schimmel and Co.[1] found that the chief constituent of estragon oil was methylchavicol, and recently their chemists, Bertram and Walbaum,[2] estimated the amount of this substance in estragon oil by Zeisel's method to be 67.8 per cent., and found that by careful oxidation paramethoxyphenylacetic acid, $C_6H_4\left\langle\begin{matrix}OCH_3\\CH_2CO_2H(p)\end{matrix}\right.$, resulted. This is the same acid that Eykman obtained by oxidizing methylchavicol. It seems highly probable, therefore, that methylchavicol and estragol are identical. This conclusion receives further confirmation from the work of Hell and Gaab,[3] who found that the methylchavicol from estragon oil, (*isoanethol*, they call it), gave a monobrom dibromide, $C_6H_3Br(OCH_3)CH_2CHBrCH_2Br$, when treated with bromine, which on oxidation yielded a ketone having the formula $C_6H_3Br(OCH_3)COCHBrCH_2Br$.

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[1] Ber. d. chem. Ges., **22**, 2736; **23**, 859.

[2] Bull. Soc. chim. (Paris), [3], **11**, 35.

Fluid Metanethol.[4]

This substance was first prepared in 1845 by Gerhardt, and again in 1863 by Kraut and Schlun by distilling anisoïn. It is a liquid with an odor resembling that of the oil of anise, and boiling at 232°.5 C., according to Kraut and Schlun. From the analyses and vapor-density determinations of the product made by him, which boiled at 206° C., Gerhardt concludes that the substance has the formula $C_{10}H_{12}O$, and is therefore a metamer of anethol. According to Kraut and Schlun, it is converted into anisoïn by the action of sulphuric acid, and into isoanethol by heating in sealed tubes to 320° C. for several hours.

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[1] Schimmel and Co.'s Bericht, 1892, 17; see also Hell, J. prakt. Chem. N. F., **51**, 424.

[2] Arch. d. Pharm., **235**, 177, (1897).

[3] Ber. d. chem. Ges., **29**, 344.

[4] J. prakt. Chem., **36**, 272; Arch. d. Pharm. (2), **116**, 241.

Anisoïn.[1]

Passing now to the substances which are probably polymers of anethol, we have first anisoïn, a resinous product made by the action of various polymerizing agents, such as sulphuric and phosphoric acids, tin and antimony chlorides, iodine and benzoyl chloride, on anethol. It is described as a white resinous solid, melting at 140°–145° C., and soluble in concentrated sulphuric acid, forming a beautiful red-colored solution, from which it is reprecipitated unchanged by the addition of water. It is said to crystallize from ether in small needles. It is unaffected by boiling with dilute acids or alkalies, and on distillation it is converted into fluid metanethol and isoanethol. No determinations of its molecular weight have as yet been recorded.

Solid Metanethol.[2]

This substance was first made in 1845 by Gerhardt, by distilling the oil of anise with tin chloride. It was more carefully studied by Perrenoud in 1877. This chemist made the product by the action of fused zinc chloride on anethol. Combustion analyses show that it is an isomer of anethol, but attempts to determine its vapor-density gave unsatisfactory results. It is described as a white, crystalline substance, melting at 132° C., and subliming slowly at 115°–120° C., not volatile with steam, and boiling above 300° C. with decomposition. The molecular weight of this isomer of anethol is also unknown.

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[1] Ann. Chim. phys. [3], **2**, 284; J. prakt. Chem., **36**, 267; Ann. Chem. (Liebig), **65**, 230: J. prakt. Chem., **77**, 490; Arch. d. Pharm. [2], **116**, 241.

[2] J. prakt. Chem., **36**, 272; Ann. Chem. (Liebig), **187**, 68.

Isoanethol.[1]

Isoanethol was prepared by Kraut and Schlun by distilling anisoïn, and also by heating fluid metanethol in sealed tubes at 330° C. for several hours. It is a pale yellow oil, resembling Venice turpentine in consistency. It is said to be stable at 380° C., is unacted on by alcoholic caustic potash solution, but is apparently partially transformed into fluid metanethol by fusion with potassium hydroxide. Both hydriodic and sulphuric acids transform it into anisoïn. Its molecular weight is unknown.

Photoanethol.[2]

This is the name given by Varda to an isomer prepared by him from anethol by the action of sunlight. It is a white, crystalline solid, melting at 207°, tasteless, odorless, nonvolatile with steam, but capable of being sublimed. The work of Varda has never been confirmed, nor have any molecular weight determinations of this isomer ever been made.

Experimental.

The anethol used was a very pure specimen, purchased from Fritzsche Bros., of New York City, members of the firm of Schimmel & Co., of Leipzig. It distilled constantly within one degree (232°–233° C. uncorr.), and melted sharply at 21°-22° C. The following analysis shows the product to be very pure:

0.3793 gram anethol gave 0.3102 gram H_2O, and 1.1250 grams CO_2.

	Calculated for $C_{10}H_{12}O$.	Found.
C	81.08	80.89
H	8.11	8.10
O	10.81	11.01

Molecular weight determinations, using the boiling-point method and the apparatus devised by Orndorff and Cameron,[3] gave the following results:

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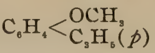
[1] Arch. d. Pharm. (2), **116**, 241.

[2] Gazz. chim. ital., **21**, 183.

[3] This JOURNAL, **17**, 517.



Anethol, $C_6H_4<\begin{matrix}OCH_3\\C_3H_5(p)\end{matrix} = 148$.

Solvent, *toluene*. Molecular elevation for 100 grams solvent, 35°.1.

I.

Grams solvent.	Grams substance.	Observed elevation.	Molecular weight found.
99.11	0.7053	0.161°	155
"	1.4246	0.289	175
"	2.0868	0.429	172
"	2.7790	0.571	172
"	3.3936	0.720	167
"	4.0585	0.856	168

Barometer, 740.1–740.3. Average, **168**

II.

Grams solvent.	Grams. substance.	Observed elevation.	Molecular weight found.
100	0.6725	0.148°	159.5
"	1.3889	0.309	158
"	1.8677	0.403	162.5
"	2.5862	0.538	169
"	3.3234	0.718	162.4

Barometer constant. Average, **162**

These results, though somewhat high, show conclusively that the molecular weight of anethol is 148, and not 296, or any higher multiple of 148, a result in accord with the vapor-density determinations. In making molecular weight determinations with liquids like anethol and some of the other products described in this paper, we introduced the liquid substance into the boiling-point apparatus in a small bulb having very thin walls (similar to those used in making combustion analyses of liquids). The condenser tube of the apparatus was narrowed a trifle (by softening it in the blowpipe flame and drawing it out a little), below the point where the solvent condensed and ran back into the flask. When the small bulbs were therefore dropped into the upper part of this condenser tube they slid down to this narrow part of the tube and either broke at once or remained there, and were broken by means of a glass rod. The bulbs were filled by means of a capillary pipette, arranged like a medicine dropper. Six or eight of these bulbs could be filled and weighed at the same time, and then be introduced into the apparatus one at a time. This method of introducing liquids into the apparatus has many advantages over the method recommended by Beckmann, not the least of which is that it is very much more accurate, as well as more convenient.

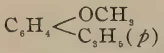
Methyl Chavicol or Estragol.

This substance was prepared from a very excellent specimen of estragon oil, purchased from Fritzsche Bros. The oil was fractionally distilled, using a short Hempel distilling-tube. A good yield of estragol, boiling constantly between 210°–212° C. (uncorr.), was thus obtained, which combustion analyses showed to be a pure product. The following are the results of the analysis:

0.3935 gram estragol gave 0.2903 gram H_2O, and 1.1702 grams CO_2.

	Calculated for $C_{10}H_{12}O$.	Found.
C	81.08	81.10
H	8.11	8.20
O	10.81	10.70

Molecular weight determinations by the boiling-point method, using the same apparatus and method of introducing the fluid substance as detailed under anethol, gave the following results:

Methyl Chavicol, 

$$C_6H_4<\begin{matrix}OCH_3\\C_3H_5(p)\end{matrix} = 148.$$

Solvent, *toluene*. Molecular elevation, 35°.1.

Grams solvent.	Grams substance.	Observed elevation.	Molecular weight found.
101.20	0.6799	0.137°	172
"	1.4536	0.299	169
"	2.0255	0.410	171
"	2.7414	0.555	171
"	3.3480	0.669	173
"	3.8781	0.784	171

Barometer, 737.9–737.8 mm. Average, **171**

These results show that the methylchavicol (or estragol), from estragon oil, has the same molecular weight as anethol, a result which might have been predicted from the fact that methylchavicol is so readily converted into anethol when heated with an alcoholic solution of caustic potash. This specimen of methylchavicol had the peculiar odor characteristic of estragon oil, and all the other properties ascribed to it by Eykman and Grimaux. It remained liquid when cooled to — 22° C., though a few crystals, which seemed to be anethol, formed on the sides of the test-tube in which the oil was cooled.

On oxidation with potassium bichromate and sulphuric acid by the method given by Ladenburg and Fitz[1] for the preparation of anisic acid from anethol it gave anisic acid, $C_6H_4\left\langle\begin{matrix}OCH_3\\COOH\ (p)\end{matrix}\right.$, though the oxidation took place less readily than in the case of anethol, and the yield of acid was much smaller. When treated with bromine in ether solution at 0° C., it readily took up one molecule of bromine, forming apparently a dibrom addition-product.[2] Hydrobromic acid was formed towards the end of the addition of the bromine, and especially on the addition of more than the one molecule of bromine. This work, together with that of other chemists on methylchavicol from estragon oil, and that made from chavicol itself, establishes the complete identity of these substances.

Fluid Metanethol.

To prepare this substance we used the best known method, namely, the distillation of anisoïn. Seventy grams of anisoïn were subjected to dry distillation in a tubulated retort, using a metal bath at first to get some idea of the temperature, and finally heating with a direct flame. The anisoïn first melts to a yellowish oil, and then slow distillation occurs at 350° C., but a temperature above 400° C. is required for rapid distillation. About sixty-six grams of the crude fluid metanethol were obtained. This was distilled in a current of steam to separate the fluid metanethol from the isoanethol formed in the reaction. The oil distilling with the water was separated,

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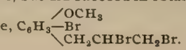
[1] Ann. Chem. (Liebig), **141**, 248.

[2] Hell and Gaab: Ber. d. chem. Ges., **29**, 344, found that it was impossible to isolate the dibromide, but did succeed in obtaining a monobrom isoanethol (methylchavicol) dibromide,  $C_6H_3\begin{matrix}/OCH_3\\—Br\\ \backslash CH_2CHBrCH_2Br.\end{matrix}$

dried with fused calcium chloride, and fractionally distilled through a short Hempel tube. The oil begins to distil at 205° C., the thermometer rising rapidly to 225° C., and then gradually to 230°, above which temperature only a small fraction remained in the flask. The greater bulk of the liquid distilled from 228°–229°, and on redistillation of the fraction 225°–230° nearly all came over between 226°–229° C. (uncor.). Analysis of this product shows that it is pure. The following are the results obtained:

0.4424 gram fluid metanethol gave 0.3305 gram H_2O, and 1.3122 grams CO_2.

	Calculated for $C_{10}H_{12}O$.	Found.
C	81.08	80.89
H	8.11	8.30
O	10.81	10.81

Molecular weight determinations by the boiling-point method gave the following results:

Fluid Metanethol, $C_{10}H_{12}O = 148$.

Solvent, *chloroform*. Molecular elevation for 100 grams, 36°.6.

Grams solvent.	Grams substance.	Observed elevation.	Molecular weight found.
184.77	0.6013	0.070°	170
"	1.4394	0.170	168
"	2.0221	0.240	167
"	2.6419	0.320	164
"	3.3052	0.400	164

Barometer, 744.7–743.5 mm. Average, **166**

These results point to a molecular weight of 148 for fluid metanethol, and show that the substance is a metamer of anethol, a result in accord with the vapor-density determinations made by Gerhardt with the product made by him, but boiling at 206° C.

Fluid metanethol is a perfectly clear, limpid, colorless oil, having an odor resembling that of oil of anise, but quite distinct from that of anethol itself. When cooled in a freezing-mixture of ice and concentrated hydrochloric acid and agitated, it solidifies to a mass of crystals, resembling crystallized anethol very closely. These crystals melt between 4° and 5° C. The freezing-point of the fluid metanethol, carefully determined with the Beckmann apparatus, was found to be 3°.1 C. When boiled with alcoholic caustic potash solution for six hours, fluid metanethol undergoes no change. The specific gravity at 20° C. was found to be 0.9852.

When oxidized with potassium bichromate and sulphuric acid, by the method of Ladenburg and Fitz,[1] it acted exactly like anethol, and gave an abundant yield of anisic acid, $C_6H_4\begin{cases}OCH_3\\CO_2H\end{cases}(p)$. When cooled to 0° C. in solution in ether and treated with bromine, it took up readily one molecule of bromine, forming a dibrom addition-product, which resembled the dibrom addition-product of anethol[2] very closely, but which melted at 63° C., and was evidently not identical with anethol dibromide.

The following are the results of the analysis of this product recrystallized from petroleum ether:

0.2094 gram substance gave 0.2543 gram AgBr.

	Calculated for $C_{10}H_{12}OBr_2$.	Found.
Br	51.9	51.7

Attempts to make fluid metanethol by other methods were unsuccessful. A small quantity is formed when anethol is distilled with fused zinc chloride, but the best method is the one given above, by the distillation of anisoïn.

Anisoïn.

Attempts to make anisoïn by the action of hydrochloric acid on anethol, as well as by the action of dilute sulphuric acid, gave unsatisfactory results. The method of Will and Rhodius was then tried and found to give practically a quantitative conversion of the anethol into anisoïn. A saturated solution of iodine in an aqueous solution of potassium iodide was prepared, and into this was slowly dropped 150 grams of pure anethol. Some unknown volatile compound appears to be formed in small quantity, which affects the mucous membranes of the eyes and nose disagreeably. The black resinous mass thus obtained was allowed to stand in contact with the iodine solution for about two hours. After draining off the iodine solution, the mass was pulverized and boiled five times with a dilute solution of potassium iodide in order partially to remove the iodine. The product was then triturated repeatedly with cold alcohol until it had acquired a pale brown hue. It was then dissolved in benzene and precipitated from the filtered solution by the addition of alcohol. It is precipitated from this solution as a gummy mass, and for this reason benzene is not to be recommended for its purification. The whole amount was now dissolved in a small quantity of ethyl acetate, and precipitated with alcohol. This treatment gave 135 grams of a pure white product, or a yield of 90 per cent., and no especial care was taken to collect all the material from the residues.

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[1] Ann. Chem. (Liebig), **141**, 248.

[2] Ladenburg: Ann. Chem. (Liebig), Spl. Bd., **8**, 94; Ber. d. chem. Ges., **2**, 372; see also Wallach: Ber. d. chem. Ges., **28**, 2714, and Hell and Günthert: J. prakt. Chem., **52**, 198.

Anisoïn was also prepared by the sulphuric acid method of Cahours.

Much time and labor were devoted to preparing pure anisoïn, but all attempts to obtain crystals of the product larger than doubtful microscopic ones, failed, although carbon disulphide, benzene, chloroform, ether, ethyl acetate, alcohol and acetone, and several combinations of these solvents were tried. The product was generally obtained when the solvent had completely evaporated, as a horn-like mass showing no evidence of crystallization. By very slowly cooling an aqueous acetone solution of anisoïn, the substance separated in small clear grains, which appeared to be crystalline to the unaided eye, but under the microscope proved to be merely rounded grains showing no crystal faces, and having no action on polarized light. They were therefore either amorphous or isotropic.

The following are the results of the analyses of the various products obtained :

I. Product melting at 181°–184°, made by the iodine method.

0.4074 gram anisoïn gave 0.2899 gram H_2O, and 1.1896 grams CO_2.

II. Product melting at 132°–140°, made by the iodine method.

0.1530 gram anisoïn gave 0.1116 gram H_2O, and 0.4463 gram CO_2.

III.[1] Product melting at 180°–192°, made by the iodine method.

IV. Product melting at 172°–190°, made by the sulphuric acid method.

0.1728 gram anisoïn gave 0.1250 gram H_2O, and 0.4997 gram CO_2.

V. Product melting at 190°–192°, made by the iodine method.

0.1705 gram anisoïn gave 0.1260 gram H_2O, and 0.5038 gram CO_2.

	Calculated for $C_{10}H_{12}O$.	Found.				
		I.	II.	III.	IV.	V.
C	81.08	79.64	79.56	79.81	78.89	80.59
H	8.10	7.91	8.10	8.04	8.04	8.21
O	10.82	12.45	12.44	12.15	13.07	11.20

Products Number I. and II. were slightly yellow, the others were pure white; I. and II. were purified by dissolving in acetic ether and precipitating by the addition of alcohol; III., IV. and V., by precipitating from acetone solution by the addition of water. Molecular weight determinations by the boiling-point method, using acetone, acetic ether, and benzene as solvents, were attempted without satisfactory results.[2] The boiling-points of these solvents remained unchanged even when over a gram of the anisoïn had been introduced. Anisoïn thus appears to be a colloid, and does not form a true solution in these solvents.

Solid Metanethol.

As Perrenoud's method for the preparation of solid metanethol gave only a small yield of the substance, attempts were made to improve the method. As these changes did not accomplish their object, it is not necessary to detail them here.

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[1] The results obtained in this analysis were lost, and only the percentage figures can therefore be given.

[2] The attempts to determine the molecular weight of anisoïn, both by the boiling-point and freezing-point methods, were made by Mr. H. J. Steuber, to whom we wish here to express our thanks.

Working according to Perrenoud's directions, 60 grams of anethol were heated in a retort with 120 grams of freshly fused zinc chloride until white fumes began to appear in the retort, when superheated steam was passed in. The solid material in the distillate was separated from the water, treated with alcohol and ether to remove unattacked anethol and fluid metanethol, and recrystallized from a mixture of absolute alcohol and chloroform, after boiling with bone-black to remove the color from the solution. A pure white product is thus obtained, but the yield is very small—only 4 grams from the 60 of anethol used. Combustion analyses of this product, melting at 123°–125° C., showed that it was not pure. The following are the results obtained :

I. 0.3305 gram solid metanethol gave 0.2362 gram H_2O, and 0.9602 gram CO_2.

II. 0.4119 gram solid metanethol gave 0.2940 gram H_2O, and 1.1976 grams CO_2.

	Calculated for $C_{10}H_{12}O$.	Found. I.	Found. II.
C	81.08	79.24	79.29
H	8.11	7.94	7.93

The product was further purified by carefully crystallizing from boiling glacial acetic acid. It now melted at 133°–133°.5 and gave the following results on analysis :

0.1922 gram substance gave 0.1422 gram H_2O, and 0.5690 gram CO_2.

	Calculated for $C_{10}H_{12}O$.	Found.
C	81.08	80.75
H	8.11	8.22
O	10.81	11.03

Attempts to determine the molecular weight of solid metanethol by the boiling-point method, using both toluene and chloroform, gave unsatisfactory results, as the substance underwent decomposition in both these solvents. Using the freezing-point method, and benzene as a solvent, the following results were obtained.

Solid Metanethol,[1] $(C_{10}H_{12}O)_2 = 296$.

Solvent, *benzene.*

Grams solvent.	Gram substance.	Observed depression.	Molecular weight found.
24.4264	0.0791	0.065°	244
"	0.1632	0.125	262
12.039	0.1180	0.173	277

These results point to the formula $(C_{10}H_{12}O)_2$ as the formula for solid metanethol. It would be better therefore to call this substance dianethol, and discard the term metanethol, which is confusing, as it is also used for the methyl ether of metapropenylphenol, $C_6H_4\begin{cases} OCH_3 \\ C_3H_5 (m) \end{cases}$.

Isoanethol.

This product was made at the same time as the fluid metanethol by the distillation of anisoïn. It was separated from the fluid metanethol by distillation in steam, remaining in the distillation-flask as a heavy viscous oil. An attempt was made to purify it by the method of Kraut and Schlun, but as this proved unsuccessful, it was subjected to fractional distillation under reduced pressure (100 mm.). A product was finally obtained boiling at 245°–255° (at 100 mm. pressure). This was a pale yellow oil of a thick syrupy consistency, which soon acquired a red color on standing. The yield was small and the product is extremely difficult to purify. An analysis gave the following results :

0.4424 gram isoanethol gave 0.3305 gram H_2O, and 1.3122 grams CO_2.

	Calculated for $C_{10}H_{12}O$.	Found.
C	81.08	80.89
H	8.11	8.38
O	10.81	11.05

Molecular weight determinations in chloroform solution by the boiling-point method gave the following results :

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[1] These determinations were made for us by Mr. H. J. Steuber, to whom we wish here to express our thanks.

Isoanethol, $(C_{10}H_{12}O)_2 = 296$.

Solvent, *chloroform*. Molecular elevation for 100 grams, 36°.6.

Grams solvent.	Grams substance.	Observed elevation.	Molecular weight found.
190.24	0.5350	0.035°	294
"	1.6477	0.100	317
"	2.2620	0.132	330
"	2.8330	0.160	341

Molecular weight at infinite dilution, **280**

Barometer, 746.1–745.9 mm.

Molecular weight determinations in toluene, by the boiling-point method, gave unsatisfactory results owing to the decomposition of the isoanethol in this solvent. Molecular weight determinations by the freezing-point method, using benzene as a solvent, gave the following results :

Isoanethol,[1] $(C_{10}H_{12}O)_2 = 296$.

Solvent, *benzene*.

Grams solvent.	Gram substance.	Observed depression.	Molecular weight found.
10.9630	0.1625	0.275°	264
"	0.3631	0.630	258
12.1770	0.1192	0.195	246
"	0.2625	0.423	248

These results show that isoanethol, like the solid metanethol, has twice the molecular weight of anethol. It would therefore be better to call this substance dianethol, and, to distinguish it from the solid metanethol, it might be called fluid dianethol, while the solid metanethol could be named solid dianethol.

Photoanethol.

Two attempts to make this substance by allowing bottles containing pure anethol to stand in the sunlight for three months, resulted unsatisfactorily. On distillation the whole amount of the liquid distilled at 232°–233° C., and only a very small amount of a tarry residue, too small to be examined, was left in the flask. A third attempt, in which the anethol was exposed for five months during the summer of 1896, gave a small amount of the photoanethol. The product was separated from the anethol by the method given by Varda. It crystallized in leaflets having a mother-of-pearl luster, and melting at 207° C. Unfortunately the amount obtained was too small for further study.

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[1] These determinations were made for us by Mr. H. J. Steuber, to whom we wish here to express our thanks.

The Action of Heat on Anethol.

As fluid metanethol results from the distillation of anisoïn, it was thought that anethol might be converted directly into its isomer, fluid metanethol, by the action of heat. Preliminary experiments showed that when anethol is heated in sealed tubes to 275°–290° C., it is completely changed. 300 grams of anethol were then heated in an autoclave for two and a half hours to 250°–275°. The pressure, as shown by the manometer, varied from seven to twelve atmospheres. No free anethol could be detected in the crude product, which had become tarry in appearance and consistency. This tarry mass was distilled in steam. The residue left in the flask, when distilled under reduced pressure, gave isoanethol. The oily distillate was separated from the water, dried and subjected to fractional distillation, a short Hempel distilling tube being used. Two fractions were isolated, one boiling at 174°–178° C., and the other at 209°–212° C.

Analyses of the fraction boiling at 174°–178° C. gave the following results:

I. 0.3477 gram of product gave 0.2576 gram H_2O, and 0.9996 gram CO_2.

II. 0.3663 gram of product gave 0.2707 gram H_2O, and 1.0537 grams CO_2.

	Calculated for $C_8H_{10}O$.	Found.	
		I.	II.
C	78.69	78.40	78.45
H	8.20	8.23	8.21
O	13.11	13.37	13.34

Molecular weight determinations by the boiling-point method gave the following results:

Product boiling at 174°–178° C., $C_8H_{10}O = 120$.

Solvent, *chloroform.*

Grams solvent.	Grams substance.	Observed elevation.	Molecular weight found.
189.25	0.9470	0.164°	112
“	1.6137	0.296	106
“	2.2167	0.393	109
“	3.1666	0.554	111
“	3.8178	0.670	110

Barometer, 735.1–735.5 mm. Average, **110**

These results show that the compound has the formula $C_8H_{10}O$. A comparison of the properties of this product with those of the methyl ether of paracresol, $C_6H_4\langle^{CH_3}_{OCH_3}(p)$, shows that the two substances are identical.

A combustion analysis of the product boiling at 209°–212° C., gave the following results:

0.3772 gram product gave 0.3142 gram H_2O, and 1.1020 grams CO_2.

	Calculated for $C_{10}H_{14}O$.	Found.
C	80.00	79.68
H	9.33	9.26
O	10.67	11.06

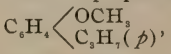
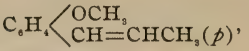
Molecular weight determinations by the boiling-point method gave the following results:

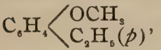
Product boiling at 209°–212° C., $C_{10}H_{14}O = 150$.

Solvent, *toluene.*

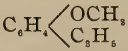
Grams solvent.	Grams substance.	Observed elevation.	Molecular weight found.
106.72	0.6996	0.137°	168
“	1.5684	0.305	169
“	2.1653	0.410	173
“	2.9004	0.548	174
“	3.7063	0.708	172

Barometer, 741.3–740.6 mm. Average, **171**

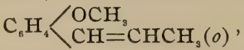
These results show that the product has the formula $C_{10}H_{14}O$. It was found to correspond in all its properties to the methyl ether of parapropylphenol,  $C_6H_4\langle^{OCH_3}_{C_3H_7(p)}$, but whether it contained the normal or the isopropyl group could not be determined, though from its method of formation from anethol,  $C_6H_4{<}\begin{matrix}OCH_3\\ CH{=}CHCH_3(p)\end{matrix}$, it is probable that it contains normal propyl.

Anethol was found to undergo the same change when boiled for a long time in a flask connected with a return condenser. It is possible that had the fractionation been conducted differently the methyl ether of paraethylphenol,  $C_6H_4{<}\begin{matrix}OCH_3\\ C_2H_5(p)\end{matrix}$, would also have been isolated from the product of the action of heat on anethol.

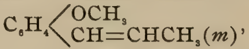
Theoretical.

A substance having the formula  $C_6H_4{<}\begin{matrix}OCH_3\\ C_3H_5\end{matrix}$ may exist in no less than fifteen metameric modifications, as follows:

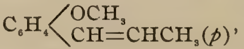
1^1-Propenylphenol-(2)-methyl ether or orthoanethol,


$$C_6H_4{<}\begin{matrix}OCH_3\\ CH{=}CHCH_3(o)\end{matrix},$$

1^1-Propenylphenol-(3)-methyl ether or metaanethol,

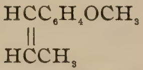

$$C_6H_4{<}\begin{matrix}OCH_3\\ CH{=}CHCH_3(m)\end{matrix},$$

1^1-Propenylphenol-(4)-methyl ether or paraanethol,

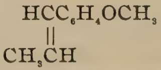

$$C_6H_4{<}\begin{matrix}OCH_3\\ CH{=}CHCH_3(p)\end{matrix},$$

the last being generally known simply as anethol.

Each of these substances could exist in two stereoisomeric modifications, the one cis, the other trans are shown in the following formulas:

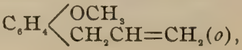

$$\begin{matrix}HCC_6H_4OCH_3\\ \|\\ HCCH_3\end{matrix}$$

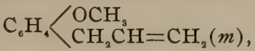
Cis-propenylphenol methyl ether.

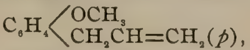

$$\begin{matrix}HCC_6H_4OCH_3\\ \|\\ CH_3CH\end{matrix}$$

Transpropenylphenol methyl ether.

Six propenylphenol methyl ethers of the above formulas are therefore possible.

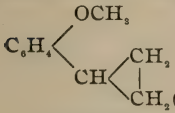
1^2-Propenylphenol-(2)-methyl ether or orthoallylphenol methyl ether,  $C_6H_4{<}\begin{matrix}OCH_3\\ CH_2CH{=}CH_2(o)\end{matrix}$,

1^2-Propenylphenol-(3)-methyl ether or metaallylphenol methyl ether, 
$C_6H_4\left\langle\begin{array}{l}OCH_3\\CH_2CH{=}CH_2\,(m),\end{array}\right.$

1^2-Propenylphenol-(4)-methyl ether or paraallylphenol methyl ether, 
$C_6H_4\left\langle\begin{array}{l}OCH_3\\CH_2CH{=}CH_2\,(p),\end{array}\right.$

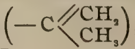
are also all possible theoretically, making nine isomers.

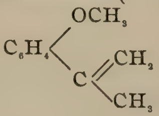
Then we may have three more isomers, ortho, meta and para, having the following structural formula,


$C_6H_4\left\langle\begin{array}{l}OCH_3\\CH\left\langle\begin{array}{l}CH_2\\ \,|\\CH_2\end{array}\right.\end{array}\right.$

(*o*), (*m*), (*p*), which might be called

1-Cyclopropenylphenol-(2), (3) and (4) methyl ether.

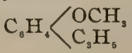
Finally we may have three isomers, ortho, meta and para containing the so-called isoallyl grouping 
$\left(-C\left\langle\begin{array}{l}{=}CH_2\\CH_3\end{array}\right.\right)$, and having the structural formula


$C_6H_4\left\langle\begin{array}{l}OCH_3\\C\left\langle\begin{array}{l}{=}CH_2\\CH_3\end{array}\right.\end{array}\right.$

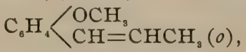
(*o*), (*m*), (*p*).

These might be named

1-Methoethenylphenol-(2), (3) and (4)-methyl ether or ortho, meta and para isoallylphenol methyl ether.

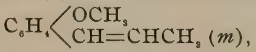
Five substances having the formula 
$C_6H_4\left\langle\begin{array}{l}OCH_3\\C_3H_5\end{array}\right.$ are now known. These are:

1^1-Propenylphenol-(2)-methyl ether or orthoanethol,


$C_6H_4\left\langle\begin{array}{l}OCH_3\\CH{=}CHCH_3\,(o),\end{array}\right.$

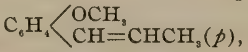
made by Perkin, and later by Mouren;

1^1-Propenylphenol-(3)-methyl ether or metaanethol,

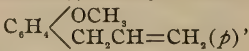

$C_6H_4\left\langle\begin{array}{l}OCH_3\\CH{=}CHCH_3\,(m),\end{array}\right.$

made by Mouren;

1^1-Propenylphenol-(4)-methyl ether or paraanethol,

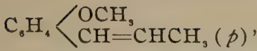

$C_6H_4\left\langle\begin{array}{l}OCH_3\\CH{=}CHCH_3\,(p),\end{array}\right.$

generally known simply as anethol;

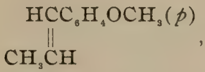
1^2-Propenylphenol-(4)-methyl ether or paraallylphenol methyl ether  $C_6H_4\left\langle\begin{array}{l}OCH_3\\CH_2CH=CH_2(p)\end{array}\right.$, called the methyl ether of chavicol by Eykman, estragol by Grimaux, and isoanethol by Hell and Gaab, and finally the substance known as fluid metanethol.

Regarding the first four of these substances the evidence upon which the above formulas are based must be considered conclusive.

The last substance, fluid metanethol, we regard as a stereoisomer of 1^1-propenylphenol-(4)-methyl ether, or ordinary anethol, for the following reasons: First, the analyses and molecular weight determinations show conclusively that its composition is correctly represented by the formula $C_{10}H_{12}O$; secondly, it gives anisic acid on oxidation, and as this substance undoubtedly has the formula $C_6H_4\left\langle\begin{array}{l}OCH_3\\COOH(p)\end{array}\right.$, fluid metanethol must be a para compound, and must contain the methoxy group, ($-OCH_3$), as well as the group, ($-C_3H_5$); thirdly, it gives with bromine very readily a dibrom addition-product, which resembles closely, but yet is different from that obtained from anethol, hence the group C_3H_5 is unsaturated and contains one double bond; fourthly, fluid metanethol undergoes no change on boiling with an alcoholic solution of caustic potash, and hence does not contain the normal allyl grouping $-CH_2-CH=CH_2$, as all compounds known to contain this grouping are changed into propenyl compounds containing the group $-CH=CHCH_3$ by this treatment. This conclusion is further justified by the fact that fluid metanethol has a higher boiling-point and melting-point than the methyl ether of paraallylphenol (estragol, methyl chavicol), substances containing the propenyl grouping invariably boiling and melting at higher temperatures than the corresponding allyl compounds. In connection with this conclusion it is perhaps well to mention here that the methyl ether of paraallylphenol (methyl chavicol, estragol), is converted into 1^1-propenylphenol-(4)-methyl ether (ordinary anethol,) on boiling with a solution of caustic potash in alcohol.

For these reasons the formula of the fluid metanethol must be  $C_6H_4\left\langle\begin{matrix}OCH_3\\ CH{=}CHCH_3\ (p)\end{matrix}\right.$, and it would be better to call the substance 1^1-propenylphenol-(4)-methyl ether, and discard the name fluid metanethol, which is old and misleading, now that the substance has been shown to be a para compound, and Mouren has made a substance which is really a metanethol. This formula is further in accord with the formation of the substance from anethol by distilling with fused zinc chloride, and by distilling the anisoïn resulting from the polymerization of anethol.

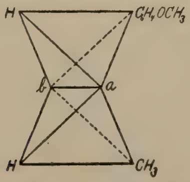
Regarding the further question as to which of these two compounds corresponds to the cis configuration and which to the trans, we are inclined to regard fluid metanethol as the trans compound,



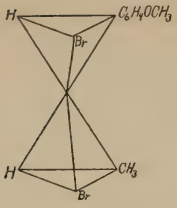
$$\begin{matrix}HCC_6H_4OCH_3(p)\\ \|\\ CH_3CH\end{matrix},$$

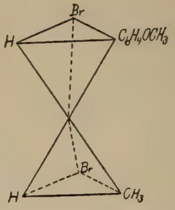
as it is formed at a high temperature, and is evidently the more stable modification at high temperatures. Further work will be necessary, however, to test this point. Assuming that it is the trans compound, it would be called trans-1^1-propenylphenol-(4)-methyl ether, while ordinary anethol would be cis-1^1-propenylphenol-(4)-methyl ether. If it be thought desirable to use shorter names, we might call fluid metanethol trans-paranethol, and ordinary anethol cis-paranethol.

The formation of two different dibrom addition-products, one from the cis- and the other from the trans-anethol is in perfect accord with these formulas. For assuming the cis formula for ordinary anethol,



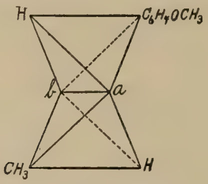
it will be seen that when bromine is added either at *a* or *b* two compounds will be formed. These are right and left

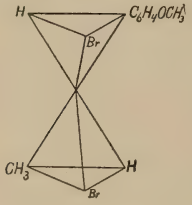


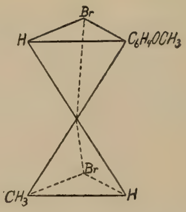


structures or enantiomorphous forms, and as both would be formed in equal amount, the product would be the inactive or racemoid type of the cisanetholdibromide.

When bromine is added to the trans compound, two dibromides will also be formed, one a right and the other a left, as shown in the formulas :



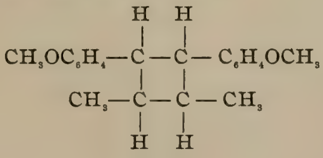




Both these substances will be formed in equal amount, and hence the product would be the racemoid type of the transanetholdibromide. It will be seen by a careful comparison of these formulas that the dibromides from cis-anethol and trans-anethol, though they should resemble each other closely, should nevertheless be different, as they are in fact, as has been shown in the experimental part of this work.

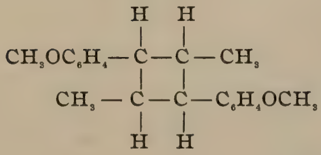
In the naming of anethol and its isomers, the method has been haphazard and bad, and the result is much confusion. The "ol" termination ought not to be used, as the substance is neither an alcohol nor a phenol. Hence such names as ortho, met- and paranethol should be discarded. Such names as ortho, meta and parapropenylanisol, which have been proposed for (*o*), (*m*) and (*p*) anethol, are also bad, first because of the "ol" termination, and secondly, because the kind of group is not sufficiently determined by the use of the word propenyl. Such names as anethoïl and anisoïl have also but little to recommend them. In this article we have, therefore, so far as possible, given the substances names in accord with the recommendations of the Geneva Conference of Chemists. These are long and cumbersome, but accurate and definite, and therefore to be preferred.

Concerning the structure of the two polymers of anethol, called isoanethol and solid metanethol, which we have shown to have twice the molecular weight of anethol, and to be really dianethols, we can say very little. Both substances seem to act like saturated compounds, so that they may be represented by formulae like these:



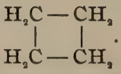
$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & \\ \mathrm{CH_3OC_6H_4} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C_6H_4OCH_3} \\ & & | & & | & & \\ \mathrm{CH_3} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{CH_3} \\ & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

and



$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & \\ \mathrm{CH_3OC_6H_4} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{CH_3} \\ & & | & & | & & \\ \mathrm{CH_3} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C_6H_4OCH_3} \\ & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

and may be derivatives of tetramethylene,



$$\begin{array}{ccc} \mathrm{H_2C} & - & \mathrm{CH_2} \\ | & & | \\ \mathrm{H_2C} & - & \mathrm{CH_2} \end{array}.$$

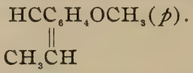
Regarding anisoïn we can only say that the molecular weight determinations in benzene, acetic ether, and acetone show that the substance does not form a true solution in these solvents.

Summary.

The results of this work on anethol and its isomers may be summed up as follows:

1. Methylchavicol of Eykman, and estragol of Grimaux, have the same molecular weight, and are metamers of anethol. From the work done on the two substances by different chemists, we must conclude that they are identical.

2. Fluid metanethol also has the same molecular weight as anethol, and is a metamer of this substance. From its chemical conduct, in which it resembles anethol very closely, and physical properties, it must be regarded as a stereoisomer of anethol, and is probably the trans compound



$$\begin{matrix}HCC_6H_4OCH_3(p).\\ \Vert\\ CH_3CH\end{matrix}$$

3. Anisoïn, the resinous polymeric modification of anethol, acts as a colloid towards the solvents, acetic ether, acetone, and benzene.

4. Solid metanethol and the liquid isoanethol both have the same molecular weight and are polymers of anethol. As their molecular weight is twice that of anethol, they should be called solid dianethol and fluid dianethol respectively. As they both act like saturated compounds, it is possible that they are derivatives of tetramethylene.

5. Names have been suggested for anethol and its isomers, which are in accord with the suggestions of the Geneva Conference of Chemists, and are more in accord with the present state of our knowledge on the subject.

6. By heating anethol under pressure to 250°–275°, it is transformed into isoanethol, the methyl ether of paracresol, $C_6H_4\left\langle\begin{matrix}OCH_3\\ CH_3(p)\end{matrix}\right.$, and the methyl ether of parapropylphenol, $C_6H_4\left\langle\begin{matrix}OCH_3\\ C_3H_7(p)\end{matrix}\right.$, the tendency under these conditions being apparently to form saturated compounds.

Further work on these substances, especially on the so-called fluid metanethol, will be undertaken in this laboratory.

CORNELL UNIVERSITY,
JUNE, 1897.

ACTION OF SULPHUR ON SILICIDES. PRODUCTION OF SILICON.

BY G. DE CHALMOT.

Action of Sulphur on Copper Silicide.

In a former article[1] I have shown that an alloy of free copper, free crystalline silicon, and copper silicide, Cu_2Si, can be obtained if silica is reduced in the presence of copper and at a very high temperature. If this alloy is treated with boiling diluted nitric acid, or with aqua regia, etc., all the copper can be dissolved and the silicon of the copper silicide will be oxidized to silica, while the free crystalline silicon remains unaltered. Hydrofluoric acid dissolves the silica, and silicon remains. This method of obtaining free silicon would be much more efficient if a large part of the silicon did not combine with the copper, being thus lost in the solutions. That this loss is quite considerable is shown by the following figures, which were obtained by the analysis of a copper silicide of average quality:

	Per cent.
Total copper	70.05
Iron	0.87
Free silicon	19.21
Combined silicon	10.10

I have tried to find a substance that will combine with the copper and react with the silicide in such a manner that the silicon is liberated according to the formula:

$$Cu_2Si + X = Cu_2X + Si.$$

I have partially succeeded in this by using sulphur. It is well known that copper and sulphur have a great affinity for each other, and that copper will even extract sulphur from iron sulphide at a temperature far below the melting-point of either substance.[2]

According to Berzelius, amorphous silicon and sulphur also react at a rather low temperature, and the reaction is even quite violent at a high temperature.

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[1] This JOURNAL, **19**, 118.

[2] Colson: Compt. rend., **93**, 74.

That sulphur would attack the copper silicide at a not too elevated temperature was likely, since copper and silicon have no great affinity for each other, a fact that is evident from the non-existence of a compound $CuSi_2$, and also from the fact that even the compound Cu_2Si will dissociate at very high temperatures, while no such reaction is known in the case of other silicides. In my experiments I mixed the well pulverized alloys with sulphur and heated them in a drying-box in closed glass tubes.

The sulphur commences to be absorbed between 200°–250° C., but the reaction is very slow. It can be completed at 270°–280° C. If the temperature is elevated much above 300° C. the reaction $Si + S_2 = SiS_2$ is much facilitated and this is detrimental to the result.

In some cases I have added just sufficient sulphur for all the copper to form cuprous sulphide, Cu_2S; in other cases I have added about twice as much, so that cupric sulphide, CuS, could be formed. In both instances, all or almost all the sulphur was absorbed, while much amorphous silicon had been liberated. The amount liberated was, however, less when more sulphur was taken. It appears that at the temperature mentioned the conditions favor the reactions:

$$2Cu + S = Cu_2S, \quad \text{and}$$
$$Cu_2S + S = 2CuS,$$

in preference to the reaction

$$Si + 2S = SiS_2.$$

In all cases, however, the reaction was not only between the copper and the sulphur. The odor of hydrogen sulphide that was given off when the product was ground up showed that some silicon and sulphur had combined, because the presence of the hydrogen sulphide can only be explained by the decomposition of the compound SiS_2 by the moisture of the air. In fact the analysis showed that only one-half to two-thirds of the combined silicon had been liberated or at least withstood the attack of the solvent liquids.

The sulphur in the mixtures, heated above its melting-point, would run together into little drops, causing a local excess of sulphur at many places, which, of course, favored the formation of silicon sulphide. I showed that this compound was formed to a considerable extent by heating the ground product with water and absorbing the hydrogen sulphide that was given off. The hydrogen sulphide was precipitated with sodium arsenate.

It is, therefore, not alone due to the action of the solvents to which the silicon is afterwards subjected that the yield is not the theoretical. In how far these solvents affect this amorphous silicon I do not know, but judging from my results and those of Vigoureux,[1] I should say that neither boiling diluted nitric acid nor hydrofluoric acid attack it to any great extent. The product obtained in the glass tube was ground up and well mixed, and a portion was used for determining the percentage of free silicon in the product. By taking into account the amount of sulphur that had been added, and the composition of the original alloy, the gain in free silicon could be calculated. In some cases sulphur would remain uncombined and stick to the sides of the tube. Its weight was taken into account, being found by dissolving sulphur in carbon disulphide. The sample taken for analysis, 1–2 grams, was treating with boiling diluted nitric acid. The residue was filtered from the copper solution, the filter and contents were dried, and the sulphur that is formed from the copper sulphide was extracted with carbon disulphide. The residue from this treatment was now carefully scraped from the filter and put into one platinum dish and the filter was cut into small pieces and put in another. Cold, strong, hydrofluoric acid was allowed to act on both filter and residue for twenty-four hours. The contents of both dishes were then filtered. The cut-up filter was washed free of acid without being brought on the filter, the washings being filtered, of course. The whole of the contents and all the filter-paper was brought in a porcelain crucible and dried, and the paper burnt, when the contents and ashes were mixed with soda potash and some saltpeter, and the insoluble silicon determined as usual. In the residue iron and copper were also determined, and their presence explained by the presence of silicides, $FeSi_2$ and Cu_2Si, and the amount of silicon required to form these compounds was deducted from the insoluble silicon to find the free silicon. There were only traces of iron and but little more copper.

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[1] Compt. rend., **120**, 369.

It was somewhat arbitrary to explain the presence of copper by assuming the presence of copper silicide. In fact, when the hydrofluoric acid acted on the residue the odor of hydrogen sulphide was quite perceptible. It is, therefore, probable that the copper was present as sulphide and that the silicon which enveloped it had prevented the nitric acid from attacking it; and that, when the sulphur was removed, the hydrofluoric acid formed the fluoride, which is quite insoluble. In that case the figures given below for free silicon in the products are too low by 0.1–0.2 per cent. There were no sulphates or only traces with the silica obtained by fusing the residue of the treatment with soda.

After having found that a large part of the combined silicon in a high-grade silicon alloy can be liberated, I also tried a low-grade alloy with the same result. In the latter case I could better examine the amorphous silicon as it is mixed with much crystalline silicon if made from high-grade silicides.

Experiment I.

5 grams high-grade silicon alloy was heated with 0.9 gram sulphur. The temperature was never over 290° C.

	Before treatment. Per cent.	After treatment with sulphur. Per cent. of original alloy.
Total silicon	29.31	....
Free "	19.21	25.77
Combined silicon	10.10	3.54
Copper	70.05	....
Iron	0.87	....

Experiment II.

5 grams low-grade silicon alloy were heated with 1.08 grams sulphur. The temperature rose to 320° C.

	Before treatment. Per cent.	After treatment with sulphur. Per cent. of original alloy.
Total silicon	12.96	....
Free "	1.22	7.84
Combined silicon	11.74	5.12
Copper	86.42	....
Iron	0.84	....

Experiment III.

5 grams of the same low-grade alloy were treated with 2 grams sulphur. The temperature was 310–330° C.

	Before treatment. Per cent.	After treatment with sulphur. Per cent. of original alloy.
Total silicon	12.96	....
Free "	1.22	6.20
Combined silicon	11.74	6.76

Experiment IV.

5 grams of the same low-grade alloy were treated with 2 grams sulphur. The temperature was kept under at 290° C.

	Before treatment. Per cent.	After treatment with sulphur. Per cent. of original alloy.
Total silicon	12.96	....
Free "	1.22	7.27
Combined silicon	11.74	5.69

The influence of the temperature becomes evident by comparing Experiments III. and IV. At 310–320° C. the amount of free silicon in the product is one per cent. less than if the temperature was only 290° C. That the larger amount of sulphur is detrimental is plain on comparing Experiments II. and especially I. with Experiments III. and IV.

Action of Sulphur on Manganese Silicide.

Manganese silicide, $MnSi_2$, is much less readily attacked than copper silicide. I have, in fact, found it impossible to obtain free amorphous silicon by heating the same with sulphur. Below 300° C. there is practically no reaction between the silicide and sulphur. I also heated a mixture of these substances in an open glass tube at the boiling-point of sulphur, and in a closed combustion tube, until the latter commenced to swell from the pressure of the sulphur vapor. In these cases I obtained products which gave the odor of hydrogen sulphide when ground up, which shows that some silicon sulphide, SiS_2, had been formed. I heated in a hard glass tube, as described, 1 gram of sulphur and 4 grams of silicide which contained: Manganese, 42.99 per cent.; free silicon, 8.26 per cent.; and an appreciable quantity of iron.

The product which had the odor of hydrogen sulphide was ground up and extracted with carbon disulphide. The residue had much the appearance of the original silicide, and contained a little insoluble sulphur. Boiling dilute nitric acid did not attack it. I therefore treated it at once with cold hydrofluoric acid, which dissolved the larger part, leaving some crystalline silicon and the insoluble sulphur. The analysis showed it to contain:

	Per cent.
Manganese	44.43
Free silicon	7.37

The relation of the amounts of manganese to free silicon before and after treatment with sulphur are as follows:

Before treatment.	After treatment.
Mn : Si = 100 : 19.2	Mn : Si = 100 : 16.6

This shows conclusively that no silicon has been liberated. In fact it appears that at the higher temperature which was required to bring about any action, the sulphur has attacked a part of the crystalline silicon.

Action of Sulphur on Chromium Silicide.

Chromium silicide, $CrSi_2$, is not acted on by sulphur at 300° C. I heated 1.30 grams sulphur with 4 grams silicide which contain 54 per cent. chromium and a trace of free silicon. The materials were well mixed. The mixture was put in a closed glass tube and was heated to 450° C. in a drying oven. There seemed to be some reaction, as all the sulphur was equally absorbed by the silicide. The product had the odor of hydrogen sulphide. When it was treated with carbon disulphide, quantities of sulphur were dissolved, and the residue looked much like the unaltered silicide. Dilute boiling nitric acid having no effect on it, it was at once treated with hydrofluoric acid. This left a small residue which contained some insoluble sulphur, some chromium, probably as sulphide, and a trace of silicon, probably due to iron silicide, $FeSi_2$. In this case also no silicon was liberated by the sulphur.

Action of Sulphur on Iron Silicide.

Iron silicide, containing 39.51 per cent. of combined and no free silicon, was boiled with sulphur in an open glass tube. The product does not have the odor of hydrogen sulphide, and the silicide remains quite unaltered.

It is shown again by these experiments that copper has much less affinity for silicon than other metals, such as iron, manganese, or chromium, and that it approaches in its conduct to silver, which only slightly combines with silicon. They also show that the affinity of copper for silicon is weak, at a high temperature when the silicide dissociates, at a low temperature when acids easily attack it, and at a medium temperature when sulphur decomposes it completely, while other silicides remain practically unaltered.

WILLSON ALUMINUM CO.,
HOLCOMB'S ROCK, VA.

ACETYLENE DIIODIDE.

BY G. DE CHALMOT.

In the *Berichte*, Vol. 30, page 1200, there is an article by Mr. H. Biltz, on acetylene diiodide C_2I_2, and ethylene tetraiodide C_2I_4. Some years ago when engaged in an entirely different line of work, I ran across acetylene diiodide, and prepared it in very much the same manner as Mr. Biltz did. I do not wish to claim any priority, for I never gave the matter much attention.

I was preparing the ethylene tetraiodide (diiodoform) by the method of Maquenne, taking calcium carbide instead of barium carbide.[1] The alcoholic washings of the crude tetraiodide were diluted with water, and the diiodide of acetylene was precipitated, together with some oily matter.

[1] Bull. Soc. chim., [3], 7, 777, 1892.

The diiodide crystallizes from alcohol or ether in long, transparent needles. I found the melting-point at 82° C. (Biltz finds 78° C.). I further found in my notes the following:

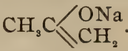
When I added iodine to a solution of acetylene in caustic potash solution, I did not obtain a trace of ethylene tetraiodide, C_2I_4, but I obtained a white precipitate. This was filtered off, and recrystallized from benzene. It forms white needles of a very pungent odor, which strangely affect the mucous membranes, especially of the eyes. An analogous compound can be made with bromine. It is an oil of very disagreeable odor. It takes fire spontaneously in contact with the air. Whether this is due to an admixture of bromacetylene, C_2HBr, or the compound itself has this property, I have not investigated.

WILLSON ALUMINUM CO.,
HOLCOMB'S ROCK, VA.

Contribution from the Laboratory of General Chemistry, University of Michigan.

THE ACTION OF SODIUM UPON METHYLPROPYLKETONE AND ACETOPHENONE.

BY PAUL C. FREER AND ARTHUR LACHMAN.

Some years ago one of us[1] showed that acetone is capable of forming a sodium derivative, whose behavior indicated the attachment of the metal to oxygen,  $CH_3C\genfrac{}{}{0pt}{}{\diagup ONa}{\diagdown CH_2}$. The chief reaction then studied showed the general analogy of the action of sodium acetone and sodium acetoacetic ether towards benzoyl chloride and towards chlorcarbonic ether, *viz.*, the simultaneous formation both of C- and O-derivatives in the first case, and of O-derivatives in the second. According to the present addition-hypothesis, this behavior finds its satisfactory explanation in the assumption of an oxy-structure of the sodium compounds. Recently[2] Freer found that acetaldehyde also forms a sodium derivative of similar structure, $CH_2{=}CHONa$. This sodium vinylate is extremely unstable, but its presence is proved by the simultaneous action of a mixture of acetaldehyde and benzoyl chloride upon finely divided sodium, resulting in the production of aldehydo-aldol benzoate,

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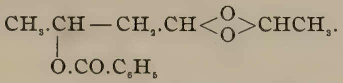
[1] This JOURNAL, **12**, 155; *Ibid*, **13**, 319; *Ibid*, **15**, 582; *Ibid*, **17**, 1.

[2] *Ibid*, **18**, 552.



$$CH_3.\underset{\underset{\displaystyle O.CO.C_6H_5}{|}}{CH}-CH_2.CH<{}^{O}_{O}>CHCH_3.$$

The existence of the above-mentioned sodium salts shows that it is by no means necessary for a methylene group to be adjacent to *two* carbonyls, in order that its hydrogen may be capable of replacement by metals. The object of the present investigation was to determine whether the property of forming sodium substitution-products is a general reaction of carbonyl compounds, or whether it is limited to the lower members of the acetone series. For this purpose, the behavior of methylpropylketone and acetophenone toward sodium was examined. The method employed was the one introduced during the study of sodium acetaldehyde, *viz.*, the combined action of the ketone and benzoyl chloride upon sodium suspended in ether.

Action of Sodium upon Methylpropylketone.

If sodium be allowed to act upon a dilute solution of methylpropylketone in ether, hydrogen is rapidly evolved, and a white, flocculent sodium compound is precipitated. This substance is fairly stable in dry air; water decomposes it immediately. Analysis shows that it has the composition represented by the formula $C_6H_9O.Na$.

1.2131 grams gave 0.8272 gram sodium sulphate.

Found, 22.1 per cent. Calculated, 21.3 per cent.

Remembering the complex nature of sodium acetone, however, it is not likely that this analogous sodium compound is a definite individual.

The action of a mixture of the ketone and benzoyl chloride upon sodium proceeds with considerable energy, so that the presence of large quantities of ether, as well as frequent cooling in water, are necessary. The reaction is usually complete within a few hours. It is best to work with about five grams of sodium wire at a time, suspended in 250 cc. of absolute ether; a mixture of 20 grams ketone and 30 grams benzoyl chloride, diluted somewhat with ether, is dropped in slowly. The product of several such reactions may be readily worked up at once. For this purpose, water is added to dissolve the yellowish solid formed, and the ether solution shaken out with dilute alkali until on acidifying no turbidity is produced in the extract. The united extracts are then treated as under *A*, and the ether residue as in *B*.

A. The Alkaline Extract.

When the alkaline extracts are acidified, a large quantity of benzoic acid separates, together with a trace of an undetermined fatty acid, and a solid polyketone. The mixture is treated with cold alcohol, which leaves the solid ketone almost completely undissolved; the alcoholic extract contains only traces of compounds other than benzoic acid.

The Solid Polyketone from Methylpropylketone.—The yield of this substance is small—13 grams from 180 grams methylpropylketone. It is almost insoluble in cold alcohol or ether, but dissolves readily in boiling alcohol. It is best purified by repeated solution in the last-named solvent, from which, however, it invariably separates in an amorphous form on cooling. A variety of solvents were tried in the attempt to obtain a crystallized body, but without a successful result, the substance always separating in white flakes, which show no regular forms, even when greatly magnified. The ketone melts in the neighborhood of 115°, with slight variations, which will be discussed below. It is very difficult to make a combustion of the substance; the highest figures obtained agree well with each other, and with the composition of *dibenzoylmethylpropylketone*.

I. 0.1789 gram gave 0.1056 gram water and 0.5057 gram carbon dioxide.

II. 0.1757 gram gave 0.1045 gram water and 0.4954 gram carbon dioxide.

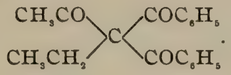
III. 0.1298 gram gave 0.0780 gram water and 0.3677 gram carbon dioxide.

	Calculated for		Found.		
	Monobenzoyl.	Dibenzoyl.	I.	II.	III.
C	75.8	77.5	77.0	76.9	77.3
H	7.3	6.1	6.7	6.6	6.7

Like all similar ketones, it colors ferric chloride intensely red. It is soluble in alkalies and carbonates, and is slowly precipitated from such solutions by carbon dioxide. Being similar in constitution to Claisen's dibenzoylacetylmethane,[1] it was expected that the new substance would likewise exist in two modifications; as a matter of fact, by varying the dilution of the alcohol used, as well as the rate at which the solution was allowed to cool, the melting-point would fluctuate between 101° and 115° and the ferric chloride reaction become occasionally very faint. But here too it was impossible to obtain crystalline products, so that nothing definite can be stated concerning the existence of the two isomers.

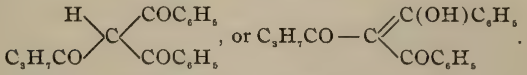
The constitution of the substance is determined by the fact that it is a dibenzoyl compound, and still possesses acid properties, of the two probable formulas, only the second corresponds to this condition:

I.



$$\begin{matrix}CH_3CO\\CH_3CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}COC_6H_5\\COC_6H_5\end{matrix}.$$

II.



$$\begin{matrix}H\\C_3H_7CO\end{matrix}\!>\!C\!<\!\begin{matrix}COC_6H_5\\COC_6H_5\end{matrix},\ \text{or}\ C_3H_7CO-C\!\begin{matrix}\diagup\!\!\diagup C(OH)C_6H_5\\\diagdown COC_6H_5\end{matrix}.$$

Saponification with alkalies proceeds only very slowly; thus, 1.031 grams were warmed on the water-bath for two full days with excess of normal caustic soda solution, of which 6.7 cc. were neutralized, while 10.5 cc. are required for complete hydrolysis. This same sample gave 0.52 gram benzoic acid instead of 0.83 gram. The small quantity of butyryldibenzoylmethane at our disposal prevented any adequate investigation thereof. With phenylhydrazine it gives several products; one of them forms long needles, melts at 110°, and contains 8.8 per cent. nitrogen.

B. The Ethereal Residue.

This contained the main products of the reaction. It was dried over calcium chloride, and distilled at 10 mm. pressure. The distillation was conducted in small portions, and continued until the distillate began to solidify, *i. e.*, consisted of benzoic acid. There always remained a large quantity of non-volatile tar (130 grams from 180 grams ketone), which decomposed when strongly heated, yielding chiefly benzoic acid. The distillate was repeatedly extracted with sodium carbonate solution, dried, and carefully refractioned five times at 10 mm., when fractions were obtained as indicated below :

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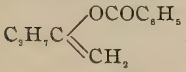
[1] Ann. Chem. (Liebig), **291**, 73.

		Grams.
I.	Below 40°	3
II.	40°–75°	1
III.	75°–90°	8
IV.	90°–111°	6
V.	112°–117°	11
VI.	Above 117°	5

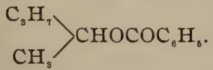
Fraction I. consisted of methylpropylketone ; *all* the others, without exception, contain chlorine. III. contained 11.4 per cent.; V. 3.2 per cent.; of an earlier preparation, the fraction corresponding to III. contained 8.5 per cent. ; that corresponding to V. contained 2.8 per cent. This chlorine is retained with the utmost tenacity ; it is not removed by repeated extraction with alkali, nor by distilling over sodium, nor finally by boiling for several days with a solution of caustic potash in methyl alcohol. The halogen is therefore present as a chlorine substitution-product. Combustions showed the various fractions to consist of mixtures.

Fraction III.—Upon saponification with a solution of caustic potash in methyl alcohol, 2 grams gave 0.9 gram benzoic acid, 1 gram methylpropylketone, a trace of unchanged halogenated oil, and an undetermined quantity of hydrochloric acid. The fraction therefore contains the isoketone benzoate,

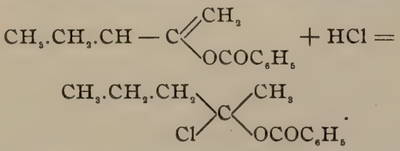


$$C_3H_7C\begin{cases}OCOC_6H_5\\ CH_2\end{cases}$$

. This is further shown by the fact that 1 gram absorbed 0.26 gram bromine without evolution of hydrobromic acid. (Calculated for pure benzoate, 0.80 gram.) No methylpropylcarbinol was observed in this fraction, the portion of the oil which does not take up bromine also yielding methylpropylketone on saponifying. This saturated compound probably consists of a hydrochloric acid addition-product of the isoketone benzoate, and will be discussed below.

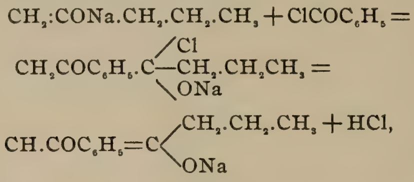
Fraction V.—The products of saponification here were as follows: 6.2 grams gave 3.2 grams benzoic acid, and undetermined quantities of hydrochloric acid, a trace of unchanged oil, and a liquid which did not react with sodium bisulphite, boiling at 114°. This liquid is therefore methylpropylcarbinol, and the fraction consists chiefly of its benzoate,  $\left.\begin{matrix}C_3H_7\\CH_3\end{matrix}\right\rangle CHOCOC_6H_5$. This again is borne out by the bromine-absorption, for 1 gram took up less than 0.3 gram thereof.

These fractions would thus seem to be mixtures inseparable by distillation; their most remarkable feature being the large amount of chlorine they contain. This chlorine could only have come from the benzoyl chloride; and as benzoyl chloride is not an active chlorinating agent, especially in the presence of an excess of sodium, the halogenated compounds can only have been formed from *intermediate addition-products*. This occurrence of halogen compounds is characteristic of all such reactions; for we have come upon the same phenomenon with acetophenone, and a preliminary trial showed quite a quantity of halogen in the product of the action of benzoyl chloride on sodium acetoacetic ether. A clue exists as to the nature of these halogenated bodies. The saponification of Fraction III. gave nothing but benzoic acid, methylpropylketone, and hydrochloric acid; the bromine-absorption showed the presence of only one-third of the *unsaturated* isoketone benzoate; the other two-thirds then consisted of the hydrochloric acid addition-product of this benzoate:



$$CH_3.CH_2.CH - C\left\langle\begin{matrix}CH_2\\OCOC_6H_5\end{matrix}\right. + HCl =$$
$$\left.\begin{matrix}CH_3.CH_2.CH_2\\Cl\end{matrix}\right\rangle C\left\langle\begin{matrix}CH_3\\OCOC_6H_5\end{matrix}\right. .$$

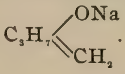
The origin of the hydrochloric acid is therefore to be sought in the breaking down of the addition-product of benzoyl chloride to sodium methylpropylketone :



$$CH_2{:}CONa.CH_2.CH_2.CH_3 + ClCOC_6H_5 =$$
$$CH_2COC_6H_5.C\begin{cases}Cl\\ -CH_2.CH_2CH_3\\ ONa\end{cases} =$$
$$CH.COC_6H_5{=}C\begin{cases}CH_2.CH_2.CH_3\\ ONa\end{cases} + HCl,$$

into *hydrochloric acid* and *sodium monobenzoyl methylpropylketone*, in accordance with Nef's hypothesis. The sodium monobenzoyl compound would then react with more benzoyl chloride to give the above described solid butyryldibenzoylmethane, again separating hydrochloric acid. The latter substance, in absolute ethereal solution, therefore, apparently more readily *adds* itself to the unsaturated isoketone benzoate than it liberates free methylpropylketone mono or dibenzoyl methylpropylketone from their sodium derivatives. That a portion of the acid is used in the latter way, is, however, proved by the fact that considerable quantities of methylpropylketones are recovered from the neutral oil. We were not able to find any monobenzoylketone, which shows that none of the latter compound was set free by the acid.

Summing up the action of benzoyl chloride upon sodium methylpropylketone, then it is in its general course similar to that with sodium acetone, and it is reasonable to ascribe a similar constitution to the sodium compounds. As the solid dibenzoylketone contains its benzoyl groups attached to the methyl, sodium methylpropylketone has the following structure:



$$C_3H_7C\begin{cases}ONa\\ {=}CH_2\end{cases}.$$

The Action of Sodium upon Acetophenone.

Some years ago, Beckmann and Paul[1] undertook the investigation of the action of sodium upon acetophenone. The compound they obtained, upon treatment with water, regenerated acetophenone, as well as acetophenone-pinacone I,

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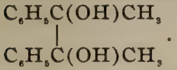
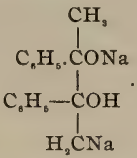
[1] Ann. Chem. (Liebig), 266, 18.



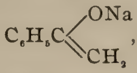
$$\begin{array}{l} C_6H_5C(OH)CH_3 \\ | \\ C_6H_5C(OH)CH_3 \end{array}$$

. Upon this as a basis, they ascribed the following formula to the substance:



$$\begin{array}{c} CH_3 \\ | \\ C_6H_5.CONa \\ | \\ C_6H_5-COH \\ | \\ H_2CNa \end{array}.$$

Such a formula, as has been pointed out in a previous paper,[1] is extremely improbable; the more so when the observation which led to it, *viz.*, the production of the pinacone with water, is readily explained by the pre-existence of sodium acetophenone-pinacone in the so-called sodium salt. As it had been previously shown by one of us[2] that sodium acetone also contains sodium pinacone, as well as sodium derivatives of higher condensation-products of acetone, it undoubtedly is true that sodium acetophenone is not a pure body. Recently Beckmann and Schliebs[3] determined the molecular weight of sodium acetophenone; they obtained no satisfactory measurements, but emphasize the fact that a *lower* molecular weight than that deduced from chemical observation was not obtained.

Our investigation of the action of sodium upon acetophenone, carried out in the manner described above, shows that acetophenone behaves just as do acetone and methylpropylketone, and that to a large extent, at any rate, sodium acetophenone is monomolecular,  , so far as can be judged from its reaction with benzoyl chloride.

105 grams of acetophenone and 120 grams benzoyl chloride, diluted with 250 cc. ether, were allowed to drop slowly upon 20 grams of sodium wire suspended in 1500 cc. ether; the ether was kept gently boiling all the while. When the odor

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[1] This JOURNAL, **15**, 582.

[2] This JOURNAL, **15**, 587.

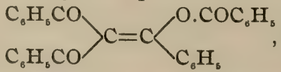
[3] Ann. Chem. (Liebig), **289**, 81, (1895).

of benzoyl chloride had disappeared, the mixture was treated with water and extracted with alkali until all soluble products had been removed.

A. Alkali Soluble Products.

The extract was acidified, and the precipitated solid extracted several times with boiling alcohol. 26 grams of crude *tribenzoylmethane* remained, which upon recrystallization from boiling acetone, melted at 223°, and showed all the characteristic reactions described by Claisen.[1] The alcoholic solution was evaporated to dryness, and then treated with dilute soda solution, whereby all except 0.5 gram was dissolved; the remainder colored ferric chloride intensely, and smelled strongly of *dibenzoylmethane*, but the amount was too small for the purification of a compound so soluble and difficult to purify. No other products could be found in the alkaline extract, except large quantities of benzoic acid.

B. Ether Solution.

This was first distilled at 14 mm. in order to remove all volatile constituents. There passed over 21 grams oil, which contained 3.8 per cent. chlorine; upon careful refractioning at ordinary pressure, it gave about 17 grams acetophenone, and a higher-boiling residue, which contained most of the halogen. The acetophenone solidified completely with phenylhydrazine, and therefore contained no phenylmethylcarbinol. The residue, after the vacuum distillation, consisted of a thick tarry mass. It was carefully saponified by allowing it to stand for a day with a solution of caustic potash in methyl alcohol, and finally warming it for a few minutes upon the water-bath. Upon acidification, the alkaline solution yielded benzoic acid and *tribenzoylmethane* (M. P. 222°, characteristic needles from acetone). The tar therefore contained among other products the benzoate of tribenzoylmethane,  $\begin{matrix}C_6H_5CO\\C_6H_5CO\end{matrix}>C=C<\begin{matrix}O.COC_6H_5\\C_6H_5\end{matrix}$, described by Claisen.

Another portion of the tar was saponified by heating it to 160° with dilute sulphuric acid for twenty hours. The products contained were *benzoic acid*, *acetophenone-pinacone* (colorless prisms, M. P., 120°.5, insoluble in soda), a *ketone* boiling at 180°–182° at 14 mm., and a large amount of tarry residue. The ketone contains halogen, colors ferric chloride deeply, is insoluble in alkalies, and reacts slowly with phenylhydrazine; it has not yet been investigated further. Particular pains were taken to find acetophenone among the products of saponification by sulphuric acid, but without success; after removing the benzoic acid, and distilling at 14 mm., the thermometer rose at once to 120°, the distillate solidifying immediately, and consisted of the pure pinacone.

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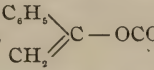
[1] Ann. Chem. (Liebig), **291**, 90.

Acetophenone thus shows the same behavior towards sodium in the presence of benzoyl chloride, as is manifested by acetone and methylpropylketone, with the exception that *no* isoketone benzoate,  $\begin{matrix} C_6H_5 \\ CH_2 \end{matrix}\!\!>\!C-OCOC_6H_5$, as would be shown by presence of acetophenone in the products of saponification, could be found.

It would seem that the more negative character of the ketone tends to suppress the formation of the O-derivatives with benzoyl chloride; thus acetone gives a considerable yield, methylpropylketone much less, acetophenone and acetoacetic ether apparently none at all. To all intents, it is a difference in degree rather than in kind of reaction.

The large quantities of tarry condensation-products seem to be the chief result of the reactions above described. For this reason the experimental investigation of other ketones scarcely promises to repay the labor necessary. However, we add a few experiments with mesityl oxide, which go to show that it is extremely probable that the property of forming sodium substitution-products is a general one with carbonyl compounds.

The Action of Sodium on Mesityl Oxide.

Pure colorless mesityl oxide, of constant boiling-point,[1] reacts so energetically with sodium that the products may even take fire with explosive violence. If the ketone is somewhat diluted with ether the action goes on more quietly. The resulting sodium compound is at first white or slightly yellow, but it soon turns to a dark red, exactly as is the case with sodium acetone. In order, if possible, to isolate the sodium compound, 1.3 grams of sodium wire were covered with absolute ether, placed in a flask with double-bored stopper, such as is described in the preparation of sodium acetone,[1] the flask was filled with pure hydrogen, covered with snow, and then an excess of mesityl oxide was gradually added. The reaction proceeded quietly and slowly, but in spite of all precautions we were not able to filter, wash and dry the sodium compound before considerable decomposition had set in, and as a consequence, no satisfactory analyses could be obtained. Warming the solution promptly turned the sodium compound deep red. A portion of the sodium compound is soluble in ether just as in the case with sodium acetone, but here also all attempts to isolate the compound failed because of the ready decomposition of the body. The sodium compound readily reacts with benzoyl chloride, the ether boils and the liquid changes to a dark-green color, which finally gives way to amber; when the latter change takes place, the action is complete. The contents of a number of flasks were united, and the ethereal solution washed with water; when the aqueous solution was acidified large quantities of benzoic acid were precipitated, as is usual with these reactions. The ethereal solution was extracted with 10 per cent. caustic potash, and the latter was supersaturated with carbon dioxide. Only a small quantity of an oil separated, and this could not be purified. On acidifying the bicarbonate solution with hydrochloric acid benzoic acid separated.

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[1] A very good yield of pure mesityl oxide is obtained by saturating acetone in a freezing-mixture with gaseous hydrogen chloride, allowing to stand for about half an hour and then pouring the liquid into ice-water. The mesityl oxide, which separates, is then washed with water and dilute alkalies, and fractioned after drying. By this

The ethereal extract was dried over calcium chloride, the ether evaporated, and the product, which contained considerable quantities of halogen, was then fractioned under reduced

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method the formation of phoron is almost completely prevented. The yield is much better than it is by Claisen's method. (Ann. Chem. (Liebig), **180**, 4.) The difference lies in not allowing the acetone to stand for any length of time after being saturated with hydrogen chloride. Acetone can be recovered from the wash-water.

[1] This JOURNAL, **15**, 588.

pressure. The first fraction contained unchanged mesityl oxide; the higher fractions were evidently condensation-products of that body; finally, above 170°, at 50 mm. pressure, large quantities of benzoic acid separated, and the distillation was interrupted. No definite substance could be separated from the lower boiling fractions. They behaved like the condensation-products of acetone. On saponification the higher portions yield benzoic acid. As the continuation with mesityl oxide did not seem to promise results of sufficient interest, further work was not undertaken. Enough has, however, been done to show that mesityl oxide behaves toward sodium much as acetone does. The difficulties in the way in the study of mesityl oxide are much greater than in that of the other ketones, owing to the ease with which it forms higher condensation-products. No better results were obtained when acetyl chloride was substituted for benzoyl.

Diethylketone, in ethereal solution, readily reacts with sodium, and a gas, which analysis proved to be hydrogen, passes off. The resulting sodium compound is white in color and its properties resemble those of the other sodium compounds prepared. Sodium diethylketone seems to be more stable than sodium acetone or sodium methylpropylketone. No further work has been done with this body.

The most curious phase of these reactions, which so far as we are aware, has never been pointed out, is the fact that large quantities of oils containing halogen are formed by the action of benzoyl chloride on the sodium derivatives of ketones, and one of us observed the same phenomenon while working with chlorcarbonic ester and sodium acetone. This fact adds to the complexity of a synthetic change which has already been the subject of so much discussion. Another feature to which attention should especially be called is the large quantity of benzoic acid which is always recovered as a result of the reactions between benzoyl chloride and sodium ketones. Evidently the halogenated bodies can only be produced by a separation of hydrogen chloride from an addition-product and its subsequent addition to the unsaturated body so produced, as was pointed out in the previous portion of this work and, very likely, the benzoic acid also takes its origin in a separation from a similar addition-product. The addition theory of Michael[1] seems now to be quite widely accepted as an explanation of the first phase of these reactions (in the cases where C-acyl compounds are produced) the difference of opinion touching the point whether the subsequent separation is one of halhydric acid or of sodium halide. The work with sodium acetone, methylpropylketone and acetophenone shows that a portion of the reaction must certainly take place with the separation of halhydric acid, because of the halogenated oils produced, but at the same time another phase of the reaction must yield benzoic acid, while it is not at all improbable that in a third direction sodium halide is also separated. With sodium acetoacetic ether the reaction does not seem to give free benzoic acid as in the acetone series, but the halogenated bodies are produced. In this case the reaction is therefore less complicated. Claisen's[2] explanation of the formation of sodium dibenzoylmethane is another phase of these reactions which undoubtedly takes place in many cases, so that we have come to the conclusion that no simple explanation will cover all the facts in any one of these reactions, and also that no general law can be deduced which will cover all cases, but that the main direction of any one reaction can only be discovered by a careful study of the particular case in question.

ANN ARBOR, JULY, 1897.

SOLUBILITY OF LEAD IN AMMONIA.

BY H. ENDEMANN.

Some years ago my attention was forcibly drawn to the possibility, that the ammonia of commerce may contain lead. Quantitative determinations of traces of lead in an organic acid were made in my laboratory, and in a western laboratory, and gave results which were low here and high in the west. My method consisted in incinerating the acid and determining the lead in the ash. The western method consisted in neutralizing the acid by ammonia, then adding ammonium sulphide, and separating and determining the lead in the precipitate thus obtained. The western method gave in my hands practically the same result as my incineration method. Meanwhile, the high results continued in the west.

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[1] J. prakt. Chem., **37**, 473.

[2] Ann. Chem. (Liebig), **291**, 54.

Inasmuch as the only reagent used in large quantity in the saturation method was ammonia, I concluded that, notwithstanding the fact that no mention had been made and published, embodying such observation, ammonia must be capable of dissolving lead in the presence of air. An experiment proved this to be correct.

The lead found in the organic acid by this method was, therefore, in part derived from the ammonia used in the analysis. Hence the difference between the results was explained.

Since, I have repeatedly had occasion to revert to this fact in one form or another, and have been unable to find any satisfactory explanation in the literature bearing upon this subject, I have finally concluded to publish my results.

In the literature but few statements can be found bearing upon the solubility of lead oxide on ammonia. The oldest statement is by Karsten, who says that lead dissolves in ammonia, forming a dark-yellow solution.

The last mention is found in the *Comptes rendus* for 1846, wherein Calvert doubts the existence of an amide of lead. Later publications are all to the effect that lead oxide is insoluble in ammonia. In all books on analytical chemistry, the statement occurs that lead salts are precipitated by ammonia "insoluble in excess."

I, myself, could not get the yellow solution of which Karsten speaks, by using litharge and the strongest ammonia in the cold, and allowing the action to proceed for weeks. I obtained no trace of lead in solution. The ammonia contained, however, some zinc, which must have been an impurity of the litharge.

If lead is immersed in the strongest ammonia (29 per cent.), there is within the first day or so, apparently no change. The ammonia remains perfectly clear and the lead shows no changes. If, however, the ammonia is tested for lead it will be found to contain quite a quantity. On allowing to stand for some time longer, the ammonia solution still remains clear, but the lead will be found coated with a colored substance. This coating is at first orange, later decidedly rust-colored as long as it remains in contact with the lead. The dark color of the coating fades quickly after the precipitate has been mechanically loosened from the metal.

After three days' action the ammonia solution contains 0.0139 per cent. lead, or 13.9 parts in 100,000 parts. The coating removed from the sheet-lead by a quick action of dilute acid, contained 0.0569 gram of lead. By allowing the action to proceed for weeks, a white precipitate is formed upon the bottom and sides of the vessel, which appears to be mainly lead hydroxide, mixed with oxides of other metals. Of ammonia, it contains only 0.15 per cent. after drying. During this long standing the ammonia had gradually become less concentrated.

If in the place of 29 per cent. ammonia, 2.9 per cent. ammonia water is taken, the oxidation of the lead is quite as lively, but the appearances differ. In twenty-four hours a white precipitate is visible upon the glass, the surface of the liquid, and upon the lead, which greatly increases during the next forty-eight hours.

The lead is partly in solution, but present mostly as precipitate. The lead in both forms together in 100 cc. of such ammonia, amounted to 0.0922 gram, or 92.2 parts for 100,000 parts of the liquid. The precipitate is also in this case apparently the hydrated oxide of lead.

The rapidity of oxidation is evidently not due to the greater or less amount of ammonia present in the experiment. In the experiment with the weaker ammonia the oxidation has been even more rapid. Whether this is due to a slightly greater surface of the lead sheets used, or to the fact that the stronger ammonia excludes the air from the flasks, and thus impedes oxidation, I have not attempted to decide. All observations tend to point to a suboxide of lead as the body soluble in ammonia; for instance, the fact that the clear solution of lead in concentrated ammonia becomes turbid on exposure to air. These observations are of considerable practical utility. In the first place, in the manufacture of ammonia water, lead linings and connections for absorption tanks should be omitted. Some such use evidently laid the foundation for my own observations. But its main importance is derived from the possible contamination of waters which have been softened by the addition of lime-water. It is a well-known fact that waters which contain bicarbonate of lime act hardly, or not at all, upon lead. To this observation may be added my own, that bicarbonate of ammonia likewise does not act upon lead. If water containing bicarbonate of lime and ammonia is softened with quicklime, the danger of destroying lead pipes becomes at once evident, if we consider that thereby the formation of some free ammonia may be caused. I should mention, however, that caustic lime is about as dangerous as ammonia. Lead dissolves quite easily in lime-water in the presence of air. Therefore, even in the absence of ammonia salts, lead may be destroyed, if proper care is not taken that the lime shall at no time be in excess.

Rain waters, which do not contain any quantity of fixed bases, but mainly ammonia salts, may at any time by loss of acid as, for instance, reduction of nitric and nitrous acid by reason of putrefaction, contain free ammonia, and then become destructive to lead while they themselves become contaminated.

In the literature we quite frequently find examples in which water apparently did not act upon lead according to the accepted notions, and in such cases it might be worth while to consider the bearings of the above facts for a probable explanation of such anomalies.

23 WILLIAM ST., NEW YORK.

THE DECOMPOSITION OF SULPHONIC ETHERS BY WATER, ACIDS AND SALTS.[1]

BY J. H. KASTLE, PAUL MURRILL, AND JOS. C. FRAZER.

Some time ago Kastle and Murrill[2] made a study of the saponification of the sulphonic ethers by alcohols. The results obtained at that time encouraged us to try the effect of water upon the sulphonic ethers, in order that a comparison might be made between it and the alcohols in the rate of change. At the outset, however, we were confronted with the difficulty that the sulphonic ethers are insoluble, or nearly so, in water. The essential preliminary, therefore, to work in this direction, was to find a solvent which would dissolve both the ether and water, and would in itself be without action on the ether. Pure acetone was finally selected as the solvent most nearly filling these requirements. This substance was found to dissolve the sulphonic ethers very readily, and to such a solution water could be added in considerable quantities without causing a precipitation of the dissolved ether. It was found, further, that the sulphonic ether could be heated with say 50 molecules of acetone, without undergoing any appreciable alteration.

The ethyl ether of *p*-brombenzenesulphonic acid was chosen for the work, as being probably the best and most available representative of this class of compounds for these experiments. This ether is readily obtained pure in considerable quantity, and is rapidly decomposed under the conditions of our experiments. The manner of conducting these experiments was as follows: The thousandth part of the molecular weight of the brom-ether in grams (0.265 gram) was dissolved in 50 gram-molecules of acetone, *viz.*, 37 cc.; and to this solution there was then added 50 times the theoretical quantity of water or ethyl alcohol, *viz.*, 0.9 cc. of water, and 2.9 cc. ethyl alcohol. These solutions were put into glass bulbs of convenient size, which were then sealed and placed in a thermostat, and kept at the desired temperature, 98° C., for different intervals of time, at the end of which the bulbs were opened and their contents titrated with $\frac{N}{10}$ caustic potash. The following results were obtained:

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[1] Abstract of a paper read before the American Association for the Advancement of Science, at the Buffalo Meeting, 1896.

[2] This JOURNAL, **17**, 290.

Table No. 1.

Time.	Water. Per cent. decomposed.	K.
20 min.	41.58	0.02723
30 “	55.44	0.02736
40 “	66.33	0.02771
50 “	74.25	0.02772
60 “	81.1	0.02776
90 “	92.1	0.02820
	Mean	=0.02766

Time.	Ethyl alcohol. Per cent. decomposed.	K.
20 min.	14.9	0.00806
30 “	20.83	0.00779
40 “	25.62	0.00739
50 “	31.49	0.00756
60 “	35.51	0.00731
70 “	40.53	0.00742
80 “	44.72	0.00740
90 “	49.74	0.00789
100 “	54.6	0.00789
120 “	57.95	0.00721
	Mean	=0.007593

On comparing the values of K for water and alcohol, it will be observed that the velocity of the reaction for water is about 3.5 times as great as that for ethyl alcohol. Such a result is in keeping with what is generally known as to the activity of these two compounds.

Action of Acids and Salts on Ethyl p-brombenzenesulphonate.

In view of the very interesting and important results obtained by Ostwald in the study of the influence of acids on the hydrolysis of methyl acetate, it was deemed expedient to make similar studies with the sulphonic ethers. Having this for their object, a number of experiments were tried as follows: 0.9 cc. of water and of normal and $\frac{N}{10}$ solutions of several acids and salts, were heated for thirty minutes in boiling water with 0.265 gram ether and 3 cc. acetone. At the end of this time the amount of decomposition was measured by titrating with $\frac{N}{10}$ caustic potash; the results of these experiments are given in Table II.

Table No. II.

Normal solutions.	Per cent.
Hydrochloric acid	26
Hydrobromic acid	21
Formic acid	63
Acetic acid	61
Butyric acid	61
½-N sulphuric acid	70
Nitrotoluene sulphonic acid	59
½-N oxalic acid	67
Calcium nitrate	55
Calcium chloride	40.5
Magnesium chloride	44.5
Sugar	67
Water	70

$\frac{1}{10}$-N Solutions.	Per cent.
Hydrochloric acid	63.31
Hydrobromic acid	63.3
Formic acid	71.5
Acetic acid	70.
Butyric acid	72.66
$\frac{1}{20}$-N sulphuric acid	70.
Potassium chloride	60.7
Sodium chloride	59.71
Sodium acetate	66.01
Potassium nitrate	66.43
Sugar	70.52
Glucose	67.9

By comparing the amount of decomposition for each substance in the above table with that of water alone, it will be observed that nearly all acids and all salts greatly retard the decomposition of the sulphonic ether—a result which is entirely at variance with those reached in the study of the hydrolysis of methyl acetate ; and one for which, for a time, no explanation could be given. It was soon found, however, that the retardation produced by acids and salts was only apparent—not real, and further, that caustic potash alone does not afford the means of measuring the decomposition of a sulphonic ether in aqueous solutions of acids and salts. An experiment with potassium iodide[1] and the brom-ether in alcoholic solution gave the clue to the correct interpretation of the above results. 0.265 gram of ethyl *p*-brombenzenesulphonate was heated for thirty minutes with 1 cc. normal solution of potassium iodide and 3 cc. alcohol. After titrating with alkali, the solution was poured into water when the characteristic odor of ethyl iodide was observed. The solution was then boiled, in order to get rid of the ethyl iodide, and titrated with $\frac{N}{10}$ silver nitrate. It took 1.9 cc. to precipitate the iodide remaining in the potassium iodide. Had all of the iodide remained unchanged, 10 cc. of $\frac{N}{10}$ silver nitrate would have been required to precipitate the iodine. Hence 81 per cent. of the potassium iodide had reacted with the sulphonic ether to form ethyl iodide and potassium *p*-brombenzenesulphonate, and only 19 per cent. of the potassium iodide remained unchanged. Similarly, it was found in the case of hydrochloric acid that this substance reacted with the sulphonic ether to form ethyl chloride and the sulphonic acid. Hence the change which takes place when an acid or a salt acts on a sulphonic ether cannot be measured by a standard solution of alkali alone. Such being the case, the results in Table II. are altogether misleading. It is really necessary to make two measurements, in order to determine what has taken place in such a solution. One, of the increase in acidity, by means of caustic potash, and another, by means of silver nitrate, of the quantity of halogen[2] which remains as halide. For at the same time that reaction is taking place between the acid or salt and the ether, decomposition also occurs between the ether and water, so that in such a solution two changes are taking place simultaneously, one according to equation (1), another according to equation (2).

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[1] Since this experiment was tried, Mr. A. S. Loevanhart has succeeded in obtaining ethyl iodide in quantity by the action of potassium iodide upon large amounts of ethyl *p*-brombenzenesulphonate, in solution in alcohol, and also in acetone, at the temperature of the water-bath, thus proving that the action of potassium iodide on a sulphonic ether is altogether analogous to its action on a salt of ethylsulphuric acid.

[2] Of course, other acids and salts, besides the halides, may react with the sulphonic ether. In fact, it is known that this is the case. In many instances, however, it would be almost impossible to measure rapidly the amount of acid or salt remaining unacted on: and hence the halide acids and salts have alone been employed in the investigation thus far, for the reason that the halogen remaining unchanged can be rapidly estimated by means of silver nitrate. We hope, in the near future, however, to try other acids and salts.

(1) $RSO_2C_2H_5 + M.Hl$[1] $= R.SO_2OM. + C_2H_6Hl.$

(2) $RSO_2OC_2H_5 + HOH = R.SO_2OH + C_2H_5OH.$

Such being the case, a number of experiments have been tried, in which both measurements have been made. In these last experiments a standard solution of the sulphonic ether in acetone was made of such concentration, that 4 cc. of it contained the thousandth part of weight in grams of the ether, *viz.*, 0.265 gram. These portions of 4 cc. each were placed in tubes of convenient size, and into each there was then introduced 1 cc. of water or a normal solution of the acid or salt. The tubes were then sealed, and allowed to remain at ordinary temperatures or heated, for the desired interval of time, at the end of which they were opened and their contents titrated, first with $\frac{N}{10}$ caustic potash, and then with $\frac{N}{10}$ silver nitrate. The results of these experiments with acids and salts are given in Tables III and IV:

Table III.

Showing the rate of decomposition of a sulphonic ether by water, acids, and salts.

Series No. 1, ordinary temperature, time, 10 days. Experiment.	$\frac{N}{10}$ caustic potash taken.		$\frac{N}{10}$ silver nitrate taken.		Percentage of ether decomposed by water.	Percentage of ether decomposed by acid or salt.	Total decomposition.
(1) With 1 cc. water	4.4	cc.	..	cc.	44.	..	44.
(2) " 1 " N-HCl	11.6	"	2.8	"	16.	72.	88.
(3) " 1 " N-HBr	11.3	"	1.8	"	13.	82.	95.
(4) " 1 " N-KI	0.8	"	0.6	"	8.	94.	102.
(5) " 1 " $\frac{N}{2}$-$MgCl_2$	2.4	"	4.4	"	24.	44.	68.
(6) " 1 " $\frac{N}{2}$-$CaCl_2$	2.5	"	4.4	"	25.	44.	69.
Series No. 2, ordinary temperature, time, 31 days.							
(1) With 1 cc. water	9.2	cc.	..	cc.	92.	..	92.
(2) " 1 " N-HCl	12.6	"	2.4	"	26.	76.	102.
(3) " 1 " N-KI	1.7	"	2.2	"	17.	78.	95.
(4) " 1 " $\frac{N}{2}MgCl_2$	3.4	"	3.25	"	34.	67.5	101.5
(5) " 1 " $\frac{N}{2}CaCl_2$	3.4	"	3.3	"	34.	67.	101.

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[1] Hl is here suggested as the proper symbol for halogen.

Series No. 3, ordinary temperature, time, 32 days. Experiment.	$\frac{N}{10}$ caustic potash taken.		$\frac{N}{10}$ silver nitrate taken.		Percentage of ether decomposed by water.	Percentage of ether decomposed by acid or salt.	Total decomposition.
(1) With 1 cc. water	9.35	cc.	..	cc.	93.5	..	93.5
(2) " 1 " N-HCl	12.5	"	2.4	"	25.	76.	101.
(3) " 1 " N-HBr	12.	"	1.8	"	20.	82.	102.
(4) " 1 " N-KI	1.95	"	2.6	"	19.5	74.	93.5
(5) " 1 " $\frac{N}{2}$-$MgCl_2$	3.3	"	3.2	"	33.	68.	101.
(6) " 1 " $\frac{N}{2}$-$CaCl_2$	3.4	"	3.2	"	34.	68.	102.
Series No. 4, temperature = 100° C., time, 40 minutes.							
(1) With 1 cc. water	8.3	cc.	..		83.	..	83.
(2) " 1 " N-HBr	11.9	"	2.	cc.	19.	80.	99.
(3)[1] " 1 " $\frac{N}{2}$-$MgCl_2$	5.1	"	6.3	"	51.	37.	88.
(4)[1] " 1 " $\frac{N}{2}$-$CaCl_2$	5.	"	7.	"	50.	30.	80.

Table IV.

Showing the decomposition of the sulphonic ether by normal hydrochloric and hydriodic acids.

Temperature 98° C. Experiment.	Time.		$\frac{N}{10}$ caustic potash taken.		$\frac{N}{10}$ silver nitrate taken.		Percentage of ether decomposed by water.	Percentage of ether decomposed by acid.	Total decomposition.
(1) With 1 cc. N-HCl	5	min.	11.	cc.	5.9	cc.	10.	41.	51.
(2) " 1 " "	10	"	11.35	"	3.9	"	13.5	61.	74.5
(3) " 1 " "	15	"	11.95	"	3.2	"	19.5	68.	87.5
(4) " 1 " "	20	"	11.8	"	2.9	"	18.	71.	89.
(5) " 1 " "	25	"	12.	"	2.5	"	20.	75.	95.
(6) " 1 " "	30	"	12.	"	2.4	"	20.	76.	96.
(1) With 1 cc. N-HI	30	min.	11.3	cc.	1.3	cc.	13.	87.	100.
(2) " 1 " "	45	"	11.2	"	1.4	"	12.	86.	98.
(3) " 1 " "	60	"	11.5	"	1.8	"	15.	82.	97.

These results are of interest first, as showing that acids and salts in solution in water and acetone decompose a sulphonic ether much more rapidly than water alone.[1] This difference in the velocity of the reaction for acids and water is in keeping with modern theoretical conceptions as to the nature of a salt or acid in solution. Being dissociated, these substances react more rapidly than water. Secondly, considerable interest attaches to these results and to this reaction, in consequence of the fact that but few chemical changes are known in which electrolytes and water react simultaneously and sufficiently slowly to enable one to follow the course of the reaction.

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[1] This is true in every substance except two. See Table III., Series No. 4, Experiments 3 and 4, and these exceptions may be due to experimental error.

As is usually the case, a rise of temperature causes a great increase in the velocity of the decomposition; in the case of hydrochloric acid, for example, as great a change occurred in twenty minutes, at 98° C., as was brought about in ten days at ordinary temperature. Further, it would seem, in some cases at least, that the distribution of decomposition between the acid and water was independent of the temperature; for example, in the case of hydrochloric acid at ordinary temperature, 72 per cent. of the ether was decomposed by the acid and 16 per cent. by water, whereas at 98° C., 71 per cent. of the ether was decomposed by the acid and 18 by water. So in the same way, in the case of hydrobromic acid, at ordinary temperature, 82 per cent. of the ether was decomposed by the acid and 20 by water; and at 100° C., in forty minutes, it was found that 80 per cent. of the ether had been decomposed by the acid and 19 per cent. by water. It will be observed further that acids and salts of analogous nature exert about the same influence upon the course of the reaction. Hydrochloric, hydrobromic, and hydriodic acids decompose the sulphonic ether to nearly the same extent; this is notably the case also with magnesium and calcium chlorides.

We have already called attention to the many interesting differences existing between the carbonic and sulphonic acids.[1] There are none more interesting, however, than that presented in the action of acids and salts on the ethers of these two types of acids. On the ethers of the carbonic acids, acids act by contact, and, without apparently suffering any decomposition themselves, greatly accelerate the action of water on the ethers; whereas, perfectly neutral salts seem to be without action upon them. On the sulphonic ethers, on the other hand, both acids and salts react in such a way as to effect a double decomposition between themselves and the ethers. In the former case the acid acts by contact; in the latter it is actually decomposed. As to the real cause of this difference in the conduct of these two types of ethers towards acids and salts, nothing of value can be said at present. In fact, no satisfactory explanation of the catalytic action of acids on the ethereal salts of the carbonic acids has ever been offered; and until we are better able to follow the part played by the acid, in its rôle as a hydrolyzing agent, speculation as to this difference in their conduct towards the carbonic and sulphonic ethers can be of little, if any, service.

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[1] Am. Chem. J., **17**, 290.

As stated in the above, one serious difficulty has stood in the way of the investigation of the decomposition of the sulphonic ethers by water and acids, and that is the insolubility of these ethers in water. Ethyl sulphonic acid, however, may be regarded as a sulphonic ether of the type represented by the formula $HO.SO_2OC_2H_5$. This compound and its salts are very soluble in water, and it is decomposed both by water and also by acids, so that it would seem to be a substance which would lend itself particularly well to the further investigations of this subject. This investigation is now in progress.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, July, 1896.

A STUDY OF ZINC HYDROXIDE IN PRECIPITATION.[1]

BY VERNON J. HALL.

Zinc hydroxide is a precipitate closely related in its nature by ferric hydroxide. Its chief difference lies in the fact that it is soluble in excess of alkali, while the latter is not. With the object in view of determining its action towards substances in solution, I have made a study of zinc hydroxide along the same line as that followed in the case of ferric hydroxide.[2]

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[1] For additional results obtained in this laboratory upon this subject, see article by Linebarger: J. Am. Chem. Soc., **17**, 354.

[2] This JOURNAL, **19**, 512.

Solutions.

In addition to the dilute solutions of potassium hydroxide and sulphuric acid mentioned in connection with the work upon ferric hydroxide, I used a solution of zinc chloride, made by dissolving 13 grams of zinc in hydrochloric acid, evaporating the excess of acid and making up to one liter with water (18½° C.). Owing to slight impurities in the zinc, I made gravimetric determinations of zinc, together with determinations of the chlorine present in this solution.

General Method.

Here, as in the work upon ferric hydroxide, the composition of the precipitate was obtained by subtracting the quantities of each constituent found in the "Filtrates" from the "Totals."

Series IV.

The first experiments were made to determine the action of zinc hydroxide upon the chlorine in a system constituted according to the following equation :

$$ZnCl_2 + 2KOH = Zn(OH)_2 + 2KCl.$$

I made up a system as follows : Into a 500 cc. flask I introduced 50 cc. of zinc chloride solution and added potassium hydroxide equivalent to two molecules, and enough more to neutralize the free acid of the solution of zinc chloride. The system thus constituted was then made up to 500 cc. with water (18½° C.). Of the mixture of solution and precipitate, well stirred, I drew off two or more portions of 50 cc. each, in which, after dissolving the precipitate with nitric acid, I made determinations of the total chlorine in the system. It will be observed that I made the determinations of chlorine in the presence of zinc. From a series of experiments previously made I have determined that zinc does not interfere in this operation. The results of these experiments are as follows :

Solution.	No zinc.	Containing zinc.	Gram.
1	0.4883	0.4897	0.1
	0.4893	0.4901	0.2
2	0.4701	0.4895	0.5
	0.4900	0.4900	0.2
	0.4896 AgCl	0.4898 AgCl	

It is seen that the average of the four results obtained with 50 cc. portions of a hydrochloric acid solution containing no zinc differ by an insignificant quantity from those containing from one-tenth to five-tenths gram of zinc.

The remainder of the mixture of solution and precipitate, after the "Totals" had been drawn off, was thrown upon a dry filter, received into a dry flask and labeled "Filtrate." Upon this duplicate determinations of chlorine were made, 50 cc. being used for each. For results see Series IV., Experiment 22. They show plainly that chlorine is not present in the precipitate when two molecules of potassium hydroxide are present.

Using the same quantity of zinc chloride as above, I proceeded to add one and one-half, one, and one-half molecules of potassium hydroxide, and to note the change, if any, in the composition of the precipitate. The method of procedure was identical with that just described for two molecules, with the addition that duplicate determinations of zinc oxide present in the "Filtrates" were made in every case. The composition of the precipitate will be seen by reference to Series IV. It will be observed that no chlorine is carried down when two molecules of potassium hydroxide are used. On the other hand, with one and one-half molecules, 7.4 per cent. of the total chlorine is present in the precipitate, and the quantity decreases as the proportion of the potassium hydroxide decreases. Two experiments were made with five and eight molecules, points at which zinc hydroxide was redissolved. For results see Experiments 26 and 27. In neither case is any chlorine carried down, although with five molecules about the same quantity of zinc hydroxide is present in the solution as was found with one and one-half molecules, the point at which the maximum quantity of chlorine appeared in the precipitate.

Series IV.

Experiment.	Mol. KOH.	ZnO in total.	ZnO in filtrate.	ZnO in precipitate.	Cl in total.		Cl in filtrate.		Cl in precipitate.	Per cent. total ZnO in precipitate.	Per cent. total Cl in precipitate.
22	2	.0798	.0000	.0798	.0700 .0701	.0701	.0699 .0698	.0699	.0000	100.00	.00
23	1½	.0798	.0142	.0656	.0703 .0701	.0702	.0650 .0649	.0650	.0052	82.2	7.4
24	1	.0798	.0366	.0432	.0705 .0704	.0705	.0659 .0659	.0659	.0045	54.1	6.4
25	½	.0798	.0562	.0236	.0701	.0701	.0676 .0676	.0676	.0025	29.6	3.6
26	5	.0798	.0148	.0650	.0706 .0704	.0705	.0704 .0702	.0703	.0000	82.4	.00
27	8	.0798	.0323	.0475	.0702	.0702	.0699 .0701	.0700	.0000	60.2	.00

Series V.

The purpose of this series was to determine the action of zinc hydroxide upon potassium sulphate and potassium chloride in a system constituted according to the following equation:

$$ZnCl_2 + 2KOH + xK_2SO_4 = Zn(OH)_2 + 2KCl + xK_2SO_4.$$

I made up a solution as follows: Into a liter flask I introduced 100 cc. of zinc chloride solution, together with the same quantity of potassium sulphate as was used in Series I. and III.; then potassium hydroxide in the proportion of two molecules, and enough more to neutralize the free acid in the zinc chloride solution. The system was then made up to 1000 cc. (18½° C.) with water, and four portions of 50 cc. each were drawn off. In two of these, after dissolving the precipitate with nitric acid, I determined the total chlorine in the system. In the remaining two I dissolved the precipitate with hydrochloric acid and determined the total sulphur trioxide present. That the presence of zinc does not interfere with the accurate determination of sulphur trioxide as barium sulphate under these circumstances is seen from the constancy of the "Totals" in this series, as well as in their close agreement with all previous "Totals." The remaining solution and precipitate were then thrown upon a dry filter, and in the "Filtrate" duplicate determinations of chlorine and sulphur trioxide were made. For results see Experiments 28 and 29. No chlorine or sulphur trioxide appears in the precipitate with two molecules.

Using the same quantity of zinc chloride and potassium sulphate, and following the same methods as just described, I determined the composition of the precipitate with one and one-half molecules. Again, as referred to in the case of ferric hydroxide, Series III., it is seen that more zinc oxide appears in the precipitate under these circumstances than at the corresponding points in Series IV., when potassium sulphate was not present in the system. The same explanation serves here as was offered in the case of ferric hydroxide. With one and one-half molecules no chlorine appears in the precipitate, but 12 per cent. of the total sulphur trioxide is carried down.

Series V.

Experiment.	Mol. KOH.	ZnO in total.	ZnO in filtrate.	ZnO in precipitate.	Cl in total.	Cl in filtrate.	Cl in precipitate.	SO_2 in total.	SO_3 in filtrate.	SO_3 in precipitate.	Per cent. total ZnO in precipitate.	Per cent. total Cl in precipitate.	Per cent. total SO_3 in precipitate.
28	2	.0798	.0000	.0798	.0705 .0705 .0705	.0705 .0706 .0706	.0000	.1158 .1157 .1158	.1143 .1142 .1143	.0000	100.00	.00	.00
29	2	.0798	.0000	.0798	....	....	....	.1159 .1157 .1158	.1154 .1153 .1154	.0000	100.00	..	.00
30	$1\frac{1}{2}$	.0798	.0054	.0744	.0703 .0703 .0703	.0701 .0701 .0701	.0000	.1159 .1157 .1158	.1021 .1018 .1020	.0138	93.2	.00	12.0

Discussion.

The argument set forth in the discussion on ferric hydroxide holds good in the case of zinc hydroxide. In no case have chlorine or sulphur trioxide and potassium appeared in the precipitate at the same time; again, neither have chlorine and sulphur trioxide appeared in the precipitate at the same time. The maximun quantity of acid, however, has uniformly appeared at a point short of two molecules where the quantity of zinc hydroxide is very little less than at complete precipitation. Here again, as in the previous discussion, we are justified in claiming for zinc hydroxide the power of decomposing substances. Further, the power of selective combination is conclusively shown in Series V., where sulphur trioxide is carried down in preference to chlorine.

Effect of Concentration.

Series VI.

It is well known that concentration plays an important part in reactions such as have been the subject of the foregoing discussion. To learn the magnitude of the disturbance brought about by concentration, I made the following experiments: I introduced 150 cc. of the zinc chloride solution into a 500 cc. flask, added potassium hydroxide in the proportion of two molecules, and proceeded to determine the chlorine in the "Totals" and "Filtrates" as in the previous work. It will be seen that all conditions here are the same as at the corresponding points in Series IV., except that the quantity of zinc chloride and potassium hydroxide in unit volume is multiplied by three. A similar experiment was also made, using one and one-half molecules. The results show a slight quantity of chlorine carried down in the case of two molecules (1.2 per cent. of the total), in this respect differing from those of the more dilute solutions in Series IV.

When one and one-half molecules are used, it is seen that the percentage of the total zinc oxide in the precipitate has decreased from 82.2 in the dilute solution in Series IV., to 81.5, and the chlorine in the precipitate has increased from 7.4 to

10.4 per cent. of the total present. Hence the tendency of concentration, so far as indicated, is to decrease the quantity of zinc oxide precipitated and to increase the quantity of chlorine carried down. In this series I examined qualitatively the basic "Filtrate" in the case of one and one-half molecules. Potassium sulphate and sodium sulphate produced a precipitate of zinc hydroxide. Acids and salts, however, other than those mentioned, produced no effect.

In addition to these experiments on zinc, two were made on iron with the same object in view. In this case again, the quantity of ferric chloride and potassium hydroxide was multiplied by three, and made up to 500 cc. "Totals" and "Filtrates" were made at corresponding points in Series II. With six molecules no chlorine appears in the precipitate. With five molecules, however, a change is noted. In the dilute solution, Experiments 16 and 17, 76.1 per cent. of the ferric oxide, and 4.5 per cent. of the chlorine were carried into precipitation. Under these conditions, however, 57.3 per cent. of the ferric oxide and 3.4 per cent. of the chlorine appear in the precipitate. In the case of iron, the tendency then of concentration is to decrease both the quantity of ferric oxide in the precipitate and the quantity of chlorine carried down. The basic solution of iron at this point gave some very interesting reactions. It was noted that upon standing the slight turbidity which often forms in a very basic solution immediately after filtration, cleared up and the solution took on a very dark red color. On the addition of a few drops of concentrated hydrochloric acid, a decided precipitate of ferric hydroxide was formed; with dilute hydrochloric acid the same; sulphuric acid, both dilute and strong, and any sulphate, cause a precipitate. Nitric acid, and nitrates other than those forming insoluble chlorides, gave no precipitate whatever; and further, sodium phosphate instead of giving ferric phosphate, produced a precipitation of all the iron in the solution in the form of ferric hydroxide.

Up to this point nothing has been said concerning potassium. In Series I. it was shown that, short of six molecules, no potassium appeared in the precipitate, but at and beyond that point potassium was carried down in very small quanti-

Series VI.

Experiment.	Mol. KOH.	ZnO in total.	ZnO in filtrate.	ZnO in precipitate.	Cl in total.		Cl in filtrate.		Cl in precipitate.	K_2O in total.	K_2O in filtrate.		K_2O in precipitate.	Per cent. total ZnO in precipitate.	Per cent. total Cl in precipitate.		Per cent. total K_2O in precipitate.
					.2095		.2073										
31	2	.2394	.0000	.2394		.2096		.2072	.0024	.2786	.2791		0	100.00	1.1		.00
					.2097		.2071									1.1	
					.2093		.2070										
32	2	.2394	.0000	.2394		.2093		.2070	.0023	....	....		..	100.00	1.1		
					.2093		.2070										
					.2096		.1876										
33	1½	.2394	.0344	.2050		.2096		.1876	.0220	....	....		..	81.5	10.4		..
					.2096		.1876										
		Fe_2O_3.	Fe_2O_3.	Fe_2O_3.													
					.3376		.3390				.4512						
34	6	.2400	.0000	.2400		.3379		.3389	.0000	.4532		.4528	0	100.00	.00		.00
					.3382		.3388				.4543						
					.3376		.3262										
35	5	.2400	.1112	.1288		.3377		.3262	.0115	.3773	.3835		0	53.7	3.4		.00
					.3378		.3262										

ties. In the last series just discussed, I made determinations of potassium in the solutions made up of ferric chloride with five and six molecules of potassium hydroxide. With the systems containing zinc chloride, however, I was unable to obtain satisfactory results, except with two molecules of potassium hydroxide. In none of these experiments was potassium found in the precipitate.

Effect of Temperature.

Series VII.

The object of this series of experiments was to determine the effect of temperature upon the phenomenon in question. I made one experiment with zinc, using one and one-half molecules of potassium hydroxide, and another with iron, using five molecules. The solutions in both cases were constituted as at corresponding points in Series IV. and Series II. respectively. The method of procedure was also the same with this exception: I divided the solution when made up into portions of 300 cc. and 200 cc., shaking thoroughly before dividing, so that the precipitate should be evenly distributed throughout the solution. From the 300 cc. portion I drew off two portions of 50 cc. each for "Totals." The remainder was filtered through a dry filter, and two portions of 50 cc. each used for the determination of chlorine in the "Filtrate." Also one portion of 50 cc. was used to determine the quantity of zinc hydroxide or ferric hydroxide, as the case might be, left in the filtrate. These determinations in "Totals" and "Filtrates" served as a check on the solution. The 200 cc. portion was boiled vigorously for five minutes in a 500 cc. flask, the mouth of which was covered with a watch crystal to prevent the escape of steam. The solution was next filtered, while hot, through a dry filter. Of this I used two portions of 50 cc. each for determinations of chlorine in the "Filtrate." Another portion of 50 cc. was used to determine the quantity of zinc hydroxide or ferric hydroxide, as the case may be, left in the "Filtrate."

The result of these experiments, as shown in Series VII., in the case of zinc, the total quantity of zinc oxide in precipita-

Series VII.

Experiment.	Mol. KOH.	ZnO in total.	ZnO in filtrate.	ZnO in precipitate.	Cl in total.	Cl in filtrate.	Cl in precipitate.	Per cent. total ZnO in precipitate.	Per cent. total Cl in precipitate.
36[1]	1½	.0798	.0136	.0662	.0707 .0706 .0705	.0642 .0642 .0642	.0064	82.9	9.00
36[2]	1½	.0798	.0240	.0558	....	.0692 .0692 .0692	.0014	69.9	1.9
		Fe_2O_3.	Fe_2O_3.	Fe_2O_3.				Fe_2O_3.	
37[1]	5	.0800	.0250	.0550	.1127 .1126 .1125	.1073 .1074 .1074	.0053	68.8	4.7
37[2]	5	.0800	.0316	.0484	....	.1111 .1110 .1109	.0016	60.5	1.4

[1] Not boiled.

[2] Boiled.

tion is reduced from 82.9 to 69.9 per cent. by boiling, and the total chlorine in the precipitate is reduced from 9.0 to 1.9 per cent.

Upon iron the general effect of boiling is the same as in the case of zinc. The total quantity of ferric oxide is reduced by boiling from 68.8 to 60.5 per cent., and the total chlorine in the precipitate is reduced from 4.7 to 1.4 per cent. The general conclusion then to be drawn from this series is that rise in temperature greatly reduces both the total metallic oxide and chlorine in the precipitate.

CHEMICAL LABORATORY, NORTHWESTERN UNIVERSITY,
EVANSTON, ILL.

REVIEWS.

THE PHASE RULE. By WILDER D. BANCROFT. The Journal of Physical Chemistry: Ithaca, New York. 1897.

Perhaps this book can be most fairly noticed by reprinting the author's preface. This course is accordingly followed: "There has been so much work done in physical chemistry during the last ten years that the mass of accumulated material is now too large to be remembered as miscellaneous facts. It becomes comparatively easy to survey the whole field if we consider the phenomena as examples illustrating a few general principles. Natural divisions of the subject are qualitative equilibrium, quantitative equilibrium, electrochemistry, and mathematical theory. The last two divisions are already recognized as sound; but the qualitative and quantitative phenomena have always been treated together, and the distinction between them has nowhere been clearly defined. My idea is that all qualitative experimental data should be presented as particular applications of the phase rule and the theorem of LeChatelier, while the guiding principles for the classification of quantitative phenomena should be the mass law and the theorem of Van 't Hoff."

"In this book I have tried to present the subject of qualitative equilibrium from the point of view of the phase rule and of the theorem of LeChatelier, without the use of mathematics. That such a treatment should be possible is due very largely to the work of H. W. Bakhuis Roozeboom, who has done far more than any one else to show the importance and significance of Gibbs's phase rule." E.

A TABULAR ATLAS OF THE CHEMISTRY OF THE METALS, comprising the arrangement on a novel plan in sectional and tabular form, devised to rapidly convey the information, of the data relating to the history, distribution, preparation, or metallurgy, properties, chemical, medical, pharmacal and technical uses, analysis and toxicology of the said metals, their organic and inorganic compounds.—METALS OF THE ALKALIES, CÆSIUM, RUBIDIUM AND POTASSIUM. BY JOHN FREMONT SLEEPER. Copyright, 1896, by the author.

Attention is here called to the beginning of an important undertaking, the preparation of a work of reference in the form of a large atlas, the subject of which is The Chemistry of the Metals. The author has been engaged upon the work for a number of years, and has his first volume now ready for publication. Publishers are, however, wary, and the author asks for subscribers, to come to his aid, $10 being the price of the volume.

There can be no doubt as to the desirability of such a work if well done. Everything depends upon its accuracy and thoroughness. Of these qualities it is impossible to judge in the case of Mr. Sleeper's Atlas, as only a few specimen pages are yet available in printed form. The general impression made by these pages is favorable, and it is to be hoped that the number of subscribers necessary to secure publication will soon be found. The amount of labor involved in the preparation of such an atlas is enormous, but this the author cheerfully faces. In a preliminary notice, after speaking of the impossibility of reaching perfection, he says: "Nevertheless, I lay this work before the public with the assurance that all has been done to render it perfect; that the most anxious care exercised by me, whose heart and soul are in the task, and who regards it as the allotted labor of his life, could effect, and that *three revisions* have been given to the more important matter it includes."

Perhaps the work is best described by calling it a somewhat mechanically-arranged, inorganic Beilstein. I. R.

NOTES ON ASSAYING. By PIERRE DE PEYSTER RICKETTS, E.M., Ph.D., and EDMUND H. MILLER, A.M., Ph.D. New York: John Wiley & Sons. 311 pp. 1897.

This is not a reprint of Prof. Ricketts' well-known *Notes on Assaying*, but is a book so much enlarged and improved that it is practically new. About one-half of the book treats of fire assays, giving the thorough and detailed instructions for which Professor Ricketts' old manual was noted. The rest of the book gives schemes of analyses of ores, laboratory tests, blowpipe analysis, and closes with a selection of tables useful to assayers. The best volumetric and electrolytic methods are given in the schemes of analysis. The book is brought up to date and will be welcomed as a worthy successor of the author's older manual. E. R.

A DETAILED COURSE OF QUALITATIVE CHEMICAL ANALYSIS OF INORGANIC SUBSTANCES WITH EXPLANATORY NOTES. By ARTHUR A. NOYES, Ph.D., Assistant Professor of Chemistry in the Massachusetts Institute of Technology. Third revised and enlarged edition. New York: Macmillan Co. 1897. 88 pp. $1.25.

The number of analytic manuals in print leads to the belief that every teacher finds it necessary to write one for his students, and to publish it for the benefit of the public at large. If each new manual were as much better than its forerunners as is that of Professor Noyes, we might hope for the speedy appearance of the ideal final manual, the last word on the subject. The author begins by letting the student mix solutions of the salts of each group in order, separating the metals. Solutions of acids are similarly studied; then dry reactions. Now the student is ready for the analysis of unknown substances. Explicit directions for analysis are given, and copious notes explain every step. All preliminary "reaction" work is omitted from this book. In his preface the author defends this omission, denies the value to the average student of a more extended acquaintance with metathetical test-tube reactions, and would substitute, time permitting, a course in inorganic preparations. To those teachers intending to write new analytic manuals, examination of this book and careful study of the preface is recommended. E. RENOUF.

JAHRBUCH DER ELEKTROCHEMIE. BERICHTE ÜBER DIE FORTSCHRITTE DES JAHRES 1896. Unter Mitwirkung der Herren Prof. Dr. K. ELBS, Giessen, Prof. Dr. F. W. KUESTER, Göttingen. Im wissenschaftlichen Theile bearbeitet von Dr. W. NERNST, o. Professor an der Universität Göttingen. Im technischen Theile bearbeitet von Dr. W. BORSCHERS, Lehrer an der Kgl. Maschinenbau- und Hüttenschule zu Duisburg. III Jahrgang. Wilhelm Knapp: Halle, A. S. 1897. pp. 347.

The size of this volume, which reviews but the work of a year, serves to call attention to the importance which electrochemistry has acquired. The scientific portion of the book fills 72 pages. The remainder of the work is devoted to the technical side. One of the most interesting developments in electrochemistry during the past year or two is in connection with the dissociating action of different solvents. J. J. Thomson first pointed out a relation between the ionizing power of solvents and their dielectric constants, and Nernst, a little later, called attention to the same relation. The recent experimental work along this line has served to make probable the conclusion of Thomson and Nernst, which gives us for the first time an insight into the physical nature or *modus operandi* of electrolytic dissociation. Other chapters of special scientific interest are on "The Theory of the Origin of the Galvanic Current," "Polarization and Electrolysis," and "Dielectric Measurements."

A misstatement of fact, for which Nernst is responsible, occurs on page 5, in connection with my error in the conductivity of solutions of acetylene in water. It is stated that G. Bredig and A. Usoff showed that the conductivity of aqueous solutions of acetylene was extremely small, and on account of impurities could scarcely be determined—"Was H. C. Jones bald darauf bestätigte, indem er die Irrthümlichkeit seiner Messungen zugab." The fact is that I corrected the error in this JOURNAL, July, 1896, and the article by Bredig and Usoff did not appear in the *Zeitschrift für Elektrochemie* until September, 1896. It is a matter of small consequence, yet perhaps it is just as well that the facts should stand on record in their true relations. The chapter on electro-analysis was written by Prof. Küster.

Some of the more interesting advances in applied electrochemistry have been in connection with the transformation of chemical energy into electrical, including the methods of obtaining electricity directly from carbon. A large number of improvements have been made also in connection with the electrolytic deposition of the metals. The organic chemist will find the chapters on the electrolysis of organic compounds, and electrolytic reductions and oxidations, written by Prof. Elbs, both instructive and suggestive. The book as a whole gives a clear and concise résumé of the advances in the many fields which are touched by electrochemistry for the year which it represents, and this is almost a necessity in the case of electrochemistry, since the literature on this subject is so scattered that it is difficult to have access to every article when it first appears.

H. C. J.

GRUNDZÜGE DER ELEKTROCHEMIE von Dr. WALTHER LÖB, Privatdocent an der techn. Hochschule zu Aachen. Mit 43 in den Text gedruckten Abbildungen. J. J. Weber, Leipzig. 1887. pp. 140.

The subject of electrochemistry is rapidly becoming enriched by a number of text-books. Those deserving especial mention are, first, that portion of Ostwald's Lehrbuch devoted to this subject, then the works of Jahn, Le Blanc, and Lüpke, all of which treat the material at hand from a somewhat different standpoint.

This brief work which the author terms a catechism of electrochemistry, deals with the subject mainly from the scientific side. The last third of the work is, however, devoted to such matters as the forms of apparatus for obtaining the current, quantitative analysis by electrolysis with description of apparatus used, electrosynthesis, etc.

The arrangement of the subject-matter is, in places, apparently not entirely in keeping with the logical method. The theory of solutions is treated before the conductivity method, which has furnished much of the evidence on which the theory rests. The law of Faraday, which is fundamental to the whole subject, is not taken up until page 112 is reached, and is then discussed rather briefly. The book is not entirely free from errors, but in general is a concise statement of some of the more important facts connected with electrochemistry.

H. C. J.

TRAITÉ ÉLÉMENTAIRE DE MÉCANIQUE CHIMIQUE FONDÉE SUR LA THERMODYNAMIQUE. Par P. DUHEM, professeur de physique théorique a la faculté des sciences de Bordeaux. Tome II. Vaporisation et modifications analogues, continuité entre l'etat liquide et l'etat gazeux, dissociation des gas parfaits. Librairie Scientifique, A. Hermann. Paris, 1898. pp. 378.

The appearance of the first volume of this work has been recently noticed in this Journal.[1] It was divided into books one and two. The second volume comprises books three, four, and five. Book three, on *Vaporization*, treats of saturated vapors, the theory of boiling, fusion and allotropic modifications, dissociation, and vaporization of a substance in two different states.

Book four on the *Continuity of the Liquid and Gaseous States*, deals with the critical point, the principle of Thomson and Maxwell's theorem, the equation of the compressibility of fluids, the specific heat of fluids, and adiabatic transformations of saturated vapors. Book five, *Dissociation in Systems which contain a Mixture of Perfect Gases*, discusses the laws of specific heat and specific volume of perfect gases, mixtures of perfect gases, dissociation in homogeneous gaseous systems, density of a dissociable gaseous combination, specific heat of such a combination, dissociation of ammonium carbamate and analogous compounds, and the dissociation of hydrogen selenide and analogous substances.

This work by M. Duhem is unquestionably the most systematic and comprehensive treatise on chemical mechanics from the mathematical standpoint, which has thus far appeared.

H. C. J.

PHYSIKALISCHE CHEMIE FÜR ANFÄNGER. von Dr. CH. M. VAN DEVENTER. Mit einem Vorwort von Prof. Dr. J. H. VAN'T HOFF. S. L. van Lovy, Amsterdam. Wilhelm Englemann, Leipzig. 1897. 167 pp.

The author states in his preface that he has endeavored to bring together the most important results in physical chemistry in such a way that this important branch of the new chemistry should be accessible to those who have not entered deeply into physics and mathematics.

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[1] This JOURNAL, **19**, 621.

The first chapter deals with such fundamental definitions as that of matter, element, etc. The second has to do with the laws of chemical combination, especially of definite and multiple proportions. In the third the laws of gases are taken up, together with a brief discussion of atoms and molecules, the constitution of molecules, and the stereochemical theories of van't Hoff and Le Bel. The fourth chapter is devoted to thermochemistry and chemical equilibrium. The principle of maximum work, which undoubtedly contains much that is true, is discussed at considerable length, and then a number of its limitations are pointed out. The fifth, sixth, and seventh chapters treat, respectively, of solutions, photochemistry and the periodic system.

The most striking omission is that of electrochemistry. This subject is barely touched upon in the chapter on solutions, under electrolytic dissociation. This is certainly not a slight omission, since no one side of physical chemistry is more interesting or important than that treated under the broad subject of electrochemistry.

The book is clearly written and comes highly recommended by van't Hoff. H. C. J.

KALENDER FÜR ELEKTROCHEMIKER SOWIE TECHNISCHE CHEMIKER UND PHYSIKER. Für das Jahr 1897. Herausgegeben von Dr. A. NEUBERGER, Redakteur der "Elektrochemischen Zeitschrift." Mit einer Beilage. Fischer's technologischer Verlag, M. Krayn. Berlin. pp. 702.

The author states that, in the preparation of this Calendar, he has had in mind especially the subject of electrochemistry. Not only the electrochemist, however, but the chemist and physicist will find this to be a useful handbook. The data compiled in these tables are of both scientific and technical value, but rather more stress seems to have been laid upon the technical side than is usually done in such work.

One can find here information in regard to the specific gravity of substances alone and in solution, the solubility of substances under varying conditions, the resistance of solids and solutions to the passage of the current; and of a more practical character under the headings, machines, combustible materials, electrochemical and electrothermal methods of producing the current, quantitative chemical electrolysis, galvano-plastic, etc.

The amount of sheer drudgery required to prepare such a work as this is easily underestimated, and it is to be hoped that this book will prove of service in many directions.

H .C. J.

TRAITÉ ELEMENTAIRE DE CHIMIE. Chimie minerale et Chimie organique. Par A. Haller et P. T. Muller. Carré et Naud. Paris, 1896.

This treatise, which is divided into two parts, the one inorganic and the other organic, is intended for the use of students working for certificates of proficiency in the natural sciences, or for candidates for scientific degrees. These books are intended for text-books alone and contain no laboratory experiments. The part devoted to general chemistry is very clear and contains a large amount of information in a compact form. There are two features of the book to which, however, objection may well be made. Before taking up the study of the simplest element the student must learn the laws of combination, laws governing combination of gases, the different methods of determining molecular and atomic weights, the meaning of valence and principles of crystallography ; while only one page in the book is devoted to a discussion of the periodic system, and that the last one in the book. The classification throughout, even among the non-metals, is based on this system ; but the relationship between the different families and elements and the important generalizations which can be drawn from a study of this arrangement of the elements is not clearly brought out or emphasized. A method of qualitative analysis is also included in this volume. The paraffins and their derivatives are treated very thoroughly in the part devoted to organic chemistry; but the attempt is made to cover the whole field and, instead of treating benzene as a type of the aromatic series, and its derivatives in a thorough manner and pointing out the relations of the more complex compounds to it, mention is made of a large number of substances and their structural formulas given without the reasons for writing them so.

J. E. G.

Correction.

Professor Peckham has called my attention to an error in my paper on California petroleum in the last number of this Journal. The oil wells in the section near Ventura, as he informs me are from five hundred to two thousand feet deep.

CHARLES F. MABERY.

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